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KELP AND OTHER SOURCES OF POTASH.*

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FERTILIZER PROBLEMS.

THE settlement and development of a country is always followed by a change, more or less gradual, from pioneer or "extensive" methods of agriculture to "intensive" methods. Such a change is now taking place in the United States, or at least in many parts of it, for the country covers so vast an area, with widely different physical and socio-economic features in its various regions, that uniform progression is impossible, and one's vision of the whole is quite apt to be occluded by local phenomena. One of the characteristics of intensive cultivation is the coincident employment of the three methods which man's ingenuity has devised for the management of the soil and the production of crops, namely: *tillage, crop rotations,* and *soil amendments,* the last being better known in this country as "fertilizers."

Of the many substances which have been found useful in increasing crop production, the experience of the world has shown among the most useful certain substances containing, or

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"carriers" of, potassium, nitrogen, and phosphorus; and, since these are not obtainable directly by the individual farmer, or require for their best utilization preliminary manipulation, there has grown up, especially in the United States and Europe, a vast business in "commercial fertilizers," which, in spite of many just criticisms and objectionable practices, has, on the whole, been a powerful and beneficient agency in advancing civilization and the development of the nation.

From the national point of view, fertilizers present three problems or groups of problems, namely: (1) the location and extent of raw materials, (2) the manufacture and distribution or sale of the manufactured products, and (3) teaching the farmer what fertilizers to use and when and how to use them. The third group of problems has received an enormous amount of attention from Federal and State agencies, the second group practically none, and the first group but very little until the last two years.

PHOSPHATES AND NITROGEN CARRIERS.

The phosphate resources of the United States are practically illimitable. There are large deposits of phosphorites or calcium phosphate in Florida, and in Tennessee, as is commonly known. Much phosphate rock still remains in the neighborhood of Charleston, S. C., although the cost of removing the overburden and mining at present has reduced the output. A number of other less important deposits are known, and in the States of Utah, Idaho, Montana, and Wyoming occurs a deposit or group of deposits of high-grade phosphorites greater than all other known deposits in the world, and capable of supplying three times the present demand for at least twelve centuries. As to nitrogen carriers, cotton-seed meal now commands too high a price as a cattle food to be used in fertilizers. The same is true of dried blood and the higher grades of tankage or slaughter-house by-products. The possible supply of ammonia from coke ovens is entirely insufficient, and no natural deposits of nitrates or ammonium salts exist in this country, so far as is now known, sufficient to meet the demands. The more general employment of leguminous crops and green manures will, however, largely meet the need for nitrogen additions to the soil, and the development of practicable methods for the fixation of atmospheric nitrogen as

cyanamide, ammonia, or nitric acid again places an illimitable supply at command.

POTASH FROM GERMANY.

The case for potassium carriers, however, has exceptionable features. In common with the rest of the world, the United States has been relying on supplies of potash from the Stassfürt mines of Germany. These mines are not inexhaustible, are subject to accident, as in the recent flooding at Jensenitz, when an appreciable percentage of the world's supply of potash disappeared over night, and are, moreover, under the control and at the disposition of a trade rival, who might some time, it is conceivable, become a belligerent rival as well. It is the part of wisdom, therefore, to find and develop an American source of soluble potash salts. Many suggestions to this end have been investigated.

MINOR POSSIBLE SOURCES OF POTASH.

Wood ashes are still brought into this country from Canada, but in steadily diminishing quantity, and the amount now is probably less than 4000 tons annually. The domestic supply is practically *nil.* There is much sawdust and waste lumber produced annually, but scattered over an immense area, and the total possible yield would be probably less than 6000 tons of potassium carbonate. *Suint* or wool washings have in times past been used in European countries. The wool cut in this country, if all washed, might yield approximately 8000 tons, but the cutting is again widely distributed and could not be profitably worked for potash on a small scale. Waste land in Russia is used to grow sunflowers, which are burnt and the ashes used as a potash fertilizer. It has been suggested that the desert regions of the United States might be utilized, but no suitable plant or methods of handling it are yet in sight. All the brines and salt wells of the country carry some small amounts of potash salts, but a careful investigation has shown conclusively that none now known can be worked economically for potash salts. In certain burnt-over areas of Nebraska, and possibly elsewhere in semi-arid areas, are ponds with no outlet or insufficient outlets which have gradually become the depositories of potassium carbonate leached from the surrounding water-shed. Some of these may be of

local value, but none, so far, give any promise of any great importance as sources of potash.

MAJOR POSSIBLE SOURCES OF POTASH.

The possible sources of potash salts above enumerated are, from a national point of view, merely minor. Recent investigations have established, however, that there are possibly four major sources of potash available in the United States. The mineral alunite, sometimes described as a natural alum, is a basic sulphate of potassium and aluminum. By heating, lixiviating, and subsequent evaporation of the resulting solution, either alum or potassium sulphate can be obtained, as may be desired. The so-called Roman alum of European commerce has long been produced thus in Italy and Spain. Alunite is widely distributed in the United States. But near Marysville, Utah, occurs a very large deposit from which it is probable that a notable quantity of potassium sulphate could be produced annually for many years to come. The deposit has not yet been sufficiently well explored to justify any attempt at quantitative estimates of its possibilities. It is now in private hands, and there is at least a reasonable expectation that it will be producing before long.

In the western and arid portion of the United States are many desert basins which in the course of time have become filled more or less with solid detrita, but which formerly were lakes receiving, in the water flowing into them, soluble potash salts as well as other dissolved material. The aggregate amount of potash salts thus accumulated in some of them must have been very large. It is possible that in the desiccation of such a lake a segregation of potash salts took place and a layer may exist somewhere below the present floor of the basin. Again, the potassium salts may be distributed through the solid fill. A 1000-foot boring in the Carson sink by the United States Geological Survey showed the water to get fresher with increasing depth. This might indicate that the salts, not being distributed, must be segregated at some lower depth. A similar 1200-foot boring by private interests in the Railroad Valley had practically the same experience. Criticisms of these views are, however, that the boring near Fallon was in the old river bed, that the Railroad Valley boring was not in the position of the valley most likely to contain salts, that there is no good reason to assume former enormous depths, that the borings already made

probably reach nearly, if not quite, to the original bottom at these points, and that laboratory experiment as well as field observation indicates that soluble salts would be found, if at all, at or near the present surface. Future investigation, perhaps requiring many years, may be necessary to determine the validity of these conflicting hypotheses. Upwards of two hundred desert basins have now been explored more or less carefully, with one certainly showing the presence of a salt body near the surface containing commercially workable quantities of potash salts. At Searles Lake, San Bernadino County, Cal., there is a playa or mud flat, about 12 square miles in area, and with an average depth somewhere between 40 and 70 feet. This "lake" is a mixture of ordinary soil material and solid salts, including sodium chloride, sodium carbonate (or carbonate and bicarbonate-trona), borax, and possibly potassium chloride, in contact with a mother liquor or brine. In the brine there is about 40 per cent. of soluble salts and approximately 6 per cent. potash. A conservative estimate of the total potassium chloride present would be 4,000,000 tons, and, especially if it is shown, as claimed, that solid potassium chloride is in the salt mixture the total amount may be much in excess of this minimum estimate. That potassium chloride may be economically produced from Searles Lake is very probable, if at the same time a market exists for the trona and borax which would be obtained in the separation. Aside from Searles Lake, the possibility of a desert basin producing potash commercially must be admitted. The probability, however, is but a speculation or the proverbial miner's chance.

Enormous quantities of potash feldspar, orthoclase or microcline, exist in this country, and in certain areas leucite, another potassium-carrying silicate. For years chemists have been working to devise methods of extracting the potash from these and similar minerals. It can, of course, be done, and quite readily, in the laboratory. It has, however, come to be recognized that no method has any commercial possibilities which does not, together with the potash or potassium salt, yield also some other salable product. At least one possibility of this kind exists. It has been found in laboratory experiments that powdered or finely-ground feldspar, when substituted for the ordinary clay or shale employed in the manufacture of cement, yields as satisfactory a clinker, and the potash is quantitatively volatilized and can be caught in the stack more or less mixed with the ordinary

flue dust. All the mechanical difficulties in catching the potash have not been satisfactorily worked out as yet, and no commercial production of potash from feldspar yet exists. But the difficulties yet to be surmounted are not formidable, apparently, and potash from feldspar is not only a possibility but a probability of the near future. So far as can now be seen, however, it must be a by-product. Not all cement mills will produce it, and quite likely it will be recovered as potash, K_2O, and will command too high a price to be available for fertilizers. On the other hand, there will probably be cases where the flue dust from cement mills will contain sufficient potash to make it valuable as a fertilizer, but where, for one special reason or another, the potash cannot be profitably extracted from the insoluble residue.

From time immemorial sea-weeds have been recognized as having an important manurial value. On many European coasts they are still so used, and on the New England coast of the United States "kelp day" is a festal occasion, when the farmers gather the torn weeds thrown upon the shores in their vicinities and haul them to their farms. In Europe certain of these marine algæ were long gathered and burned, the ashes being known as kelp, a term sometimes applied to the green plants also. These ashes had a considerable value for their iodine content, and the "kelp rights" on the coast of Brittany especially, as well as in certain sections of Ireland, Scotland, Norway, the Hebrides, the Shetlands, and some other vicinities, were of great importance.[1] Besides their remarkable power of abstracting iodine from sea-water, sea-weeds generally show another phenomenon, in abstract-

[1] In the course of time the iodine business centered in Glasgow, Scotland, and into the hands of a few firms who sent out ships to the points cited above to collect kelp. At present Japan supplies her own needs in iodine from kelp, and has done so since the beginning of her war with Russia. The rest of the world, however, has long been supplied with iodine obtained from the mother liquors resulting from the recrystallization of Chili saltpeter, the control of the business yet remaining in Glasgow. The present price of iodine (about $1.90 per pound) is an artificial one and could probably be greatly reduced, as it is reported that the possible production in Chili is far in excess of the world's demands. The giant kelps of the Pacific coast all contain iodine, though not in as high proportion as many other sea algæ. They could produce annually a hundred times the average consumption of the United States (about two hundred and fifty tons), but unless new uses for iodine are discovered or extremely cheap methods of extraction are devised there appears to be very little prospect for "iodine from kelp" competing successfully with the Chilian product.

ing relatively large amounts of potassium from the sea, although the latter is very dilute with respect to this element and quite highly concentrated with respect to its chemical analogue sodium. To the large content of potassium is usually attributed the manurial value of sea-weeds, although the easily digestible nitrogen and readily decomposable organic substances they contain probably have much to do with their value.

THE GIANT KELPS OF THE PACIFIC COAST.

Introduction.—On the Pacific coast of North America occur a number of different sea-weeds and rock weeds. Three of the brown algæ are known locally as the "Giant kelps." These are *Nereocystis luetkeana, Macrocystis pyrifera,* and *Pelagophycus porra.* They are characterized by the exceptionally high content of potassium, some five times, on the average, the content of the better-known Atlantic algæ.[2] These giant kelps occur in numerous beds or groves, often of great extent, and are beyond question an ample, perennial *possible* source of potash for the present needs of the United States.

The credit for recognizing the value and importance of the Pacific giant kelps as a source of potassium is due to Mr. David M. Balch,[3] of Coronado Beach, who in several journal notices as well as patents called attention not alone to the high content of potassium in these plants, established by careful analysis, but to their vast aggregate amount; and pointed out possible methods

[2] That high content of potassium may be found in other algæ is, of course, recognized. A sample of "Sea lettuce" gathered by Captain Crandall near Point Loma, and analyzed recently by Dindemuth and Merz, contained 30 per cent. potash (K_2O), or 47.4 per cent. potassium chloride, out of 57.1 per cent. total soluble salts. There were also present in the dried sample 32.8 per cent. organic matter and 1.7 per cent. nitrogen.

[3] Mr. Balch's principal publication appeared in the *Journal of Industrial and Engineering Chemistry,* in 1909, vol. i, p. 777.

His work on the Pacific Kelps, the labors of years, has as yet brought him neither the financial nor scientific rewards its importance so richly merits. Advanced years and uncertain health have caused him to cease active work on this subject, although his interest is yet as keen as ever, as the writer can testify from recent personal interviews and an active correspondence. It is a privilege to have this opportunity of recording appreciation for and calling attention to the amiable personality and important public services of this pioneer in the development of a great natural resource of the nation, and especially of his adopted State of California.

of manipulation for their commercial exploitation. Balch's work, however, failed to attract attention. Meanwhile, working under a process devised by the late Dr. Firmin, of San Diego, The Coronado Chemical Company was attempting to prepare a product or products by fusing kelp and natural phosphorites, lixiviating the melt, and subsequent crystallization from the resulting solution. The process failed to develop commercial possibilities and has been abandoned. Other more or less desultory efforts to utilize kelp on a commercial scale were made from time to time.[4] For instance, Mr. Andrews, of San Diego, prepared a beautiful paper from it, and serious consideration was at one time given to a plan to prepare fibre from the yucca very common on the arid deserts of Southern California, to be worked into paper, with kelp as a raw material for the binder and filler.

Samples of kelp and potassium chloride prepared therefrom by Mr. Balch were called to the writer's attention and examined in September, 1910. As nothing definite was known at that time regarding the extent of these marine growths, no further attention was given to the matter, especially as neither money, authority, nor opportunity then existed for an investigation. Some time later, when the investigation of the fertilizer resources of the United States had been inaugurated, the results of this examination were recalled, and steps were taken to make a recognizance survey of the extent of the kelp groves and to collect representative samples for analysis and confirmation of Balch's data. During the summer of 1911 field observations were made by Prof. Geo. B. Rigg on Puget Sound, by Prof. Frank M. McFarland of the coast from the Golden Gate to Point Sur, and by Captain W. C. Crandall of the coast from Cape Conception to Point Loma. Laboratory investigations at Washington of the samples collected, together with these field studies, showed the giant kelps of the Pacific coast[5] to be an ample and satisfactory possible

[4] One of the most interesting products obtained from kelp is a conserve much resembling candied citron, which Prof. T. C. Frye, and C. E. Magnuson, of Washington University, Seattle, prepare by leaching out the potassium and sodium salts and then steeping the residue in cane-sugar solution containing lemon or any other desired flavoring. The product coming from the sea, being first made in Seattle and much resembling citron, has been named "Seatron." It has apparently great merits and should some time find a good market.

[5] For details of this work, see Senate Document No. 190, Sixty-second Congress, Second Session, 1912.

source of potash. The work was continued in 1912, and, as a result, working maps have been prepared of kelp groves aggregating 230 square miles, from and including the United States shore line of Puget Sound to the Cedros Islands, Mexico. A large number of samples were collected and analyzed, and observations made having an importance for the development of a "potash from kelp" industry. This present year two parties are at work locating and determining the extent and important characteristics of the kelp along the Alaskan shore line. A third party is investigating on the ground the possibilities of developing a combined fish scrap and kelp industry on Puget Sound and in Alaska, and important laboratory investigations are in progress at Washington, D. C. Observations are also being made at La Jolla and Point Firmin, Cal., and at Friday Harbor, Wash., on factors in the life-history of these algæ of importance to their utilization commercially, and more especially to the effects upon the stand of cutting over and harvesting kelp.

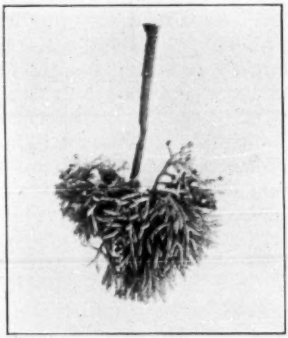
Distribution of Kelp.—In the Puget Sound region and as far south as Point Sur, on the California coast, the principal kelp is the nereocystis. Macrocystis also occurs, usually in a band outside the nereocystis and, of course, in deeper water. From Point Sur southwards nereocystis practically disappears. The macrocystis occurs in large groves or beds, often several miles in extent and from a few yards to two or more miles in width. Along the outer edge of the macrocystis, in scattered groups or individual plants, occurs the pelagophycus. The pelagophycus has probably the highest content of potassium, but does not occur in sufficient quantities to give it any great commercial importance.[6]

Conditions for Growth.—The conditions for growth for all three species of giant kelps are similar in that there must be a rocky bottom and a continuous and considerable movement of the water. The kelps have no root system as land plants in the sense of a mechanism for absorbing a solution of substances needed for their metabolism; but they have a group of tentacle-like branches, much resembling in outward appearance a root system, known as the "holdfast," which surrounds a rock, pebble, or other heavy and more or less permanent object, and thus anchors the plant. Inasmuch as the plants often grow to a very

[6] Pelagophycus is the kelp employed in the manufacture of curios familiar to tourists in Southern California. The business is but a minor one, aggregating a few thousand dollars annually.

large size, much oxygen and carbon dioxide are required by it, and, being submerged, it must obtain these constituents from the supply dissolved in the sea-water. Consequently new masses of water must be continually supplied. In the Puget Sound region and along the island-studded coast of Alaska nereocystis is likely to be found wherever there is a fairly rapid tide movement over a rocky bottom. The depth of water may be only two or three feet up to several fathoms. Macrocystis is found on exposed coasts where there is a continual swell. It grows at three fathoms and less in small patches, but the larger groves are usually at depths of from six fathoms at the shore side to ten

FIG. 1.



A holdfast of nereocystis.

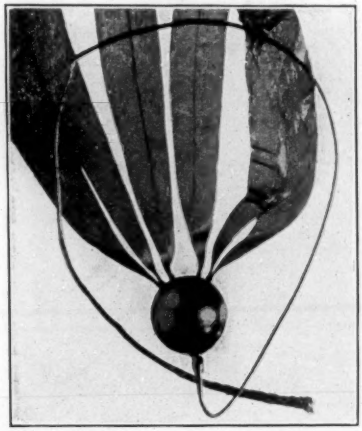
fathoms at the seaside. Pelagophycus is usually found at depths of from eight to fourteen fathoms.

The giant kelp groves are what a forester would call practically pure stands. They are all chlorophylous plants with leaves floating on the surface, for which they are provided with special floating devices, the pneumatocysts. Their tissues are practically fibreless, but quite turgid, and lose from 80 to 85 per cent. when dried. Nereocystis has a long, hollow stipe from the holdfast to the pneumatocyst, which is a hollow, sphere-like contrivance about six inches, more or less, in diameter, with a fleshy wall of perhaps an inch or less in thickness. This bulb floats with the tide, and from it stream out a leaf or leaves relatively narrow,

but some leaves of great length. It is sometimes known locally as ribbon kelp, sometimes as bull kelp.

Pelagophycus is like nereocystis in having a long, hollow stipe from the holdfast, ending in a spherical pneumatocyst. But the pneumatocyst of pelagophycus is two or more times wider than with the nereocystis, and from it spring horn-like stipes, ending in leaves. Because of the horn-like branches this kelp is commonly known as elk kelp; sometimes also it is called bull

FIG. 2.



Young nereocystis plant, showing pneumatocyst and basal splitting of leaves.

kelp, probably from confusion with nereocystis, because of the prominence of the spherical pneumatocyst on the end of a long stipe in both plants.

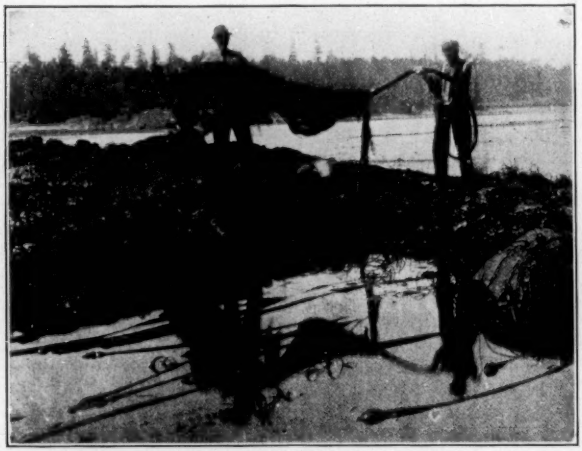
Macrocystis has a somewhat different manner of growth and quite a different appearance. From the holdfast spring a number of stipes, often branched and usually from 80 to 100 feet in length.[7] Along these stipes spring fronds, each leaf carrying at its base and connecting it to the stipe a small, hollow

[7] Much greater lengths are by no means unusual, and the enormous length of 1000 feet has been reported.

pneumatocyst which floats it. The leaf would probably average 12 to 14 inches in length, three to four inches at its widest, and is serrated. The pneumatocyst is roughly ovoid in shape, about two inches in length and three-fourths of an inch in diameter of widest cross section.

Period of Growth.—Nereocystis is an annual. It is propagated by spores which are developed in certain spots or areas

FIG. 3.



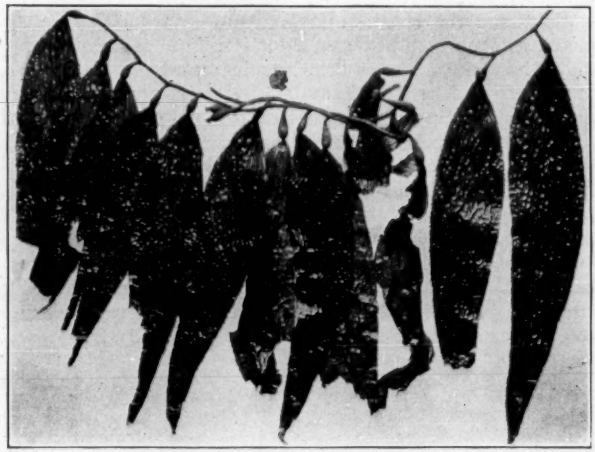
Rock near Turn Island at low tide. The two men are holding a nereocystis plant. The rocks on which they are standing are covered with alaria.

on the leaf and are ripe, in the Puget Sound region, about the middle of July. If cutting of the groves becomes extensive it may be desirable to establish a closed season until July 15 or perhaps a week or two later, to prevent a "killing out" of the groves. The other alternative is to permit early cutting, but under supervision and control, so that a fair percentage of vigorous plants may mature to "reseed" the grove. Until further and more definite knowledge of the life-history of the plant is at hand, and certainly until after a kelp industry is

actually established, it is of doubtful wisdom to formulate or enact any restrictive legislation, although such has been proposed.

Macrocystis has a life-history certainly longer than a calendar year, and is probably a perennial. It also grows from spores, but these develop, generally, on leaves at considerable depths below the surface. It seems altogether improbable that cutting over the groves of this plant, even to depths of two fathoms, could produce any permanent injury. It is popularly supposed that a cut macrocystis stipe will continue to grow, and that a cut-over

FIG. 4.



Macrocystis pyrifera from Southern California.

grove will be restored to its former condition in from 40 to 60 days. Recent observations made specifically to obtain information on this point appear to show clearly that when a stipe of macrocystis is cut decay sets in at the injured surface and progresses slowly toward the holdfast. Because of the mechanical stimulation, or from some unknown reason, however, cutting induces new stipes to be sent out from the holdfast, or a branching of the old stipes, so that an effect is produced on the plant

akin to or similar to the well-known "stooling" of wheat. Be the explanation what it may, areas cut over near Point Loma and Point Firmin were less than a year later much heavier and thicker in growth.

Loss of Potash from Dead Kelp.—Kelp, when cut and allowed to lie in the water, soon loses its high content of potash. Drift kelp contains but little. It is certain that the leaching commences at once after cutting, and that various schemes of harvesting which have been proposed, such as towing the floating kelp in nets or allowing it to wash ashore in the surf and then gathering it on the beach, are fundamentally incorrect in principle, and the kelp should be removed from the sea and drained as soon as practicable after it is cut. Moreover, even though lying in a strong brine, as in sea-water, the cut kelp soon shows evidences of decay, and large masses of putrescent kelp are neither easy nor pleasant to handle.

To obtain some definite evidence of the rate at which the potassium chloride leaches from the cut kelp, Captain Crandall cut samples of kelp and hung them overboard during a cruise of the yacht *Agazzi*, of the Scripps Biological Institute, La Jolla, Cal., cutting out sub-samples from the leaching kelp from time to time, and sending them to Washington. The samples were in somewhat putrescent state when they arrived, but were dried as quickly as possible and then analyzed by Messrs. Lindemuth and Merz, with the results given in Tables I and II.

TABLE I.

ANALYSES OF KELP GATHERED NEAR CORONADOS ISLAND, APRIL 16, 1913, 2:30 P.M., AND REMAINING IN THE WATER FOR VARIOUS LENGTHS OF TIME.

Date	Time	K_2O. Per cent.	Soluble salts. Per cent.	Organic matter. Per cent.	Ash. Per cent.	Nitrogen. Per cent.
April 16.....	2:30 P.M.	12.48	31.46	65.38	3.16	0.98
April 16.....	2:30 P.M.	13.47	31.26	65.98	2.76	.79
April 16.....	5:30 P.M.	15.56	34.00	62.38	3.62	.95
April 16.....	8:30 P.M.	17.30	38.26	58.66	3.08	1.00
April 17.....	4:30 A.M.	17.64	38.30	58.30	3.40	1.07
April 17.....	7:30 A.M.	13.35	31.96	54.96	3.08	.83
April 17.....	10:30 A.M.	10.74	26.36	70.66	2.98	.90
April 16[1].....	2:30 P.M.	18.28	36.78	60.86	2.36	.51
April 16[2].....	2:30 P.M.	9.90	25.94	70.18	3.88	.84

[1] Stems only. [2] Leaves only.

TABLE II.

ANALYSES OF KELP GATHERED NEAR POINT LOMA, CALIFORNIA, APRIL 18, 1913, 4 P.M., AND REMAINING IN THE WATER FOR VARIOUS LENGTHS OF TIME.

Date	Time	K_2O, Per cent.	Soluble salts, Per cent.	Organic matter, Per cent.	Ash, Per cent.	Nitrogen, Per cent.
April 18.....	4 P.M.	15.82	40.88	47.32	11.80	2.77
April 18.....	7:30 P.M.	13.43	34.82	56.54	8.64	2.66
April 19.....	7:30 A.M.	14.96	37.66	52.76	9.58	2.40
April 19.....	10:30 A.M.	13.05	34.34	60.12	5.54	1.77
April 19.....	1:30 P.M.	11.00	30.22	62.52	7.26	1.85
April 19.....	4:30 P.M.	11.59	30.52	59.92	9.56	2.10
April 19.....	7:30 P.M.	13.68	38.94	50.56	10.50	2.22
April 20.....	7:30 A.M.	10.31	27.84	62.38	9.78	1.97
April 20.....	10:30 A.M.	16.39	38.78	53.30	7.92	2.22
April 20.....	1:30 P.M.	11.77	32.44	60.54	7.02	1.99
April 20.....	4:30 P.M.	16.69	39.72	54.22	5.96	1.79
April 20.....	7:30 P.M.	15.77	40.80	45.88	13.32	2.29
April 21.....	7:30 A.M.	16.74	42.58	45.36	12.06	2.49
April 21.....	10:30 A.M.	16.75	38.64	55.28	6.08	1.91
April 21.....	4:30 P.M.	14.67	35.58	58.12	6.30	1.88
April 21.....	7:30 P.M.	12.61	34.74	55.46	9.80	2.66
April 22.....	7:30 A.M.	15.54	40.84	48.92	10.24	2.47
April 22.....	10:30 A.M.	17.62	41.42	49.48	9.10	2.16
April 22.....	1:30 P.M.	17.03	42.44	44.50	13.06	2.28
April 22.....	4:30 P.M.	15.61	37.80	54.42	7.78	2.16
April 22.....	7:30 P.M.	20.28	46.28	43.96	9.76	2.12
April 23.....	7:30 A.M.	15.72	38.80	51.44	9.76	2.26
April 24.....	7:30 A.M.	15.60	39.24	48.74	12.02	2.57
April 23.....		15.27	34.52	57.42	8.06	1.80

These results show no consistent trend, and it appears probable that for some time after cutting and until the individual cells of the plant tissues have died the loss of potassium from the cut kelp is relatively slow.

Drying of Kelp.—All the giant kelps, when cut and exposed to the air, lose water quite readily. The tissue shrivels and on the surface appears an incrustation or efflorescence of the salt mixture, mainly potassium and sodium chlorides, the former predominating decidedly. This salt mixture is easily shaken off the dried plant.[8] But, although kelp, when freely exposed to the air, loses water and dries quickly, green kelp, when allowed to lie in heavy wet masses, quickly packs to a sticky, slimy mass of

[8] It is said that nereocystis freshly cut and almost immediately dried in an oven on a fairly large scale, in some practical experiments made at Port Townsend, Wash., did not exhibit any efflorescence nor lose any salt when shaken.

putrescent material, with a most offensive odor and most attractive to flies.

Experience has apparently demonstrated that in commercial practice, except possibly on the Mexican coast line, it will be desirable to dry the kelp by artificial means. Various schemes for this purpose have been proposed, but apparently the most practical and efficient would be a rotary cylinder, with lengthwise baffle plates, to break up the kelp masses, the cylinders set at a slant and a current of hot dry air being passed through it. The kelp, cut into short lengths, is fed by a hopper into the upper end and the dried product falling from the lower end removed by endless conveyor or any appropriate means. The whole device is quite similar to the familiar ordinary cement kiln or modern lime furnace, except that a current of hot dry air, instead of a naked flame, is blown through. Similar dryers are used for desiccating fish scrap and such like materials, dry porous rock, and even for evaporating brines. Dryers of this type which can be reasonably expected to handle kelp very efficiently are now on the market and can be procured at very reasonable prices.

Composition of Kelp.—The composition of the kelp tissue is not at all satisfactorily known. It probably differs considerably with different species and varieties. A few definite substances have been isolated, and a number of "algins" and "alginic acids," etc., for whose definite existence there is no satisfactory evidence, although some of the properties of the actual masses of these hypothetical individuals are very interesting and possibly of considerable technical importance. Confining attention, however, to the fertilizer possibilities, a considerable mass of data has now been accumulated regarding the giant kelp.

The composition of the giant kelps as regards their fertilizer constituents has been determined, at least approximately, now by numerous analyses by Balch, Turrentine, Lindemuth, and Parker. In Tables III, IV, and V are given results obtained by Turrentine or Lindemuth and Parker on samples of oven-dried kelp (105° C.) which appeared to be fair average specimens and selected otherwise only as regards their distribution along the coast. The averages in these tables do not, however, accord very closely with those obtained by Parker and Lindemuth[9] from

[9] *Journal of Industrial and Engineering Chemistry*, 5, 287 (1913).

TABLE III.

COMPOSITION OF NEREOCYSTIS.

Location	K_2O, Per cent.	I. Per cent.	N. Per cent.	Organic matter, Per cent.
Fresh Water Bay, Puget Sound	18.04	0.23	2.26	51.13
	17.61	.24	2.21	51.11
	31.62	.25	1.21	33.15
	16.92	.20	2.57	51.16
	17.05	.24	2.71	51.67
	17.32	.28	2.53	50.12
	16.20	.19	2.54	52.14
	16.50	.30	2.21	37.40
	16.72	.20	1.46	39.02
San Juan County, Wash	25.70	.08	1.29	41.80
	13.30	.15	2.52	61.50
	23.00	.17	1.32	46.20
	16.20	.15	2.32	35.30
Point Arena, Cal	16.72	.13	2.22	53.56
	20.62	.15	2.25	51.42
Bay of Monterey, Cal	16.96	.20	2.15	57.25
	23.82	.17	2.41	47.26
	21.70	.18	1.58	50.20
Point Pinos, Cal	19.40	.12	1.70	53.00
	26.10	.15	1.12	40.60
Cayucos, Cal	20.83	.24	1.93	47.86
Average	19.63	0.19	2.02	47.75

a consideration of all the existing analytical data, including good, bad, and indifferent specimens. Their averages are probably more reliable approximations, and from them the following conclusions may be drawn.

(1) No definite quantitative relations exist between the different constituents of kelp.

(2) The potassium content of nereocystis is greater than that of macrocystis.

(3) The potassium content of northern kelp is higher than that of the southern kelp.

(4) There is no positive difference in iodine content between northern and southern kelps.

So far as results obtained are available, the following conclusions also seem justified:

(5) The proximity of the mouth of a fresh-water stream has no appreciable effect on the potash and nitrogen content of kelp.

TABLE IV.

COMPOSITION OF MACROCYSTIS.

Location	K_2O, Per cent.	I, Per cent.	N, Per cent.	Organic matter, Per cent.
Low Point, Wash.	12.80	0.23	1.37	59.40
Neah Bay, Wash.	19.60	.20	1.81	51.50
Pillar Point, Cal.	17.26	.15	2.18	58.14
	27.66	.14	1.00	41.04
Santa Cruz, Cal.	16.44	.24	2.16	59.80
Monterey Bay, Cal.	18.30	.26	2.32	57.00
	12.38	.18	2.11	68.80
Point Aulon, Cal.	23.00	.32	1.83	51.20
Point San Luis, Cal.	8.62	.14	2.35	68.26
Rocky Point, Cal.	9.35	.25	2.72	73.06
Point Conception, Cal.	14.17	.24	2.15	62.95
San Miguel Island	16.40	.29	1.54	50.60
Santa Cruz Island	17.40	.32	1.57	49.40
Anacapa Island	12.60	.26	.95	64.40
Cape Quemada, Cal.	14.10	.29	.90	63.50
Goleta Point, Cal.	16.70	.17	1.00	56.70
Point Las Pitos, Cal.	12.30	.20	.98	66.20
La Jolla Point, Cal.	13.60	.38	1.04	64.40
Point Medanos, Cal.	13.40	.23	.74	62.90
Point Loma, Cal.	15.70	.15	.90	60.90
Average	15.59	0.23	1.58	59.51

TABLE V.

COMPOSITION OF PELAGOPHYCUS.

Location	K_2O, Per cent.	I, Per cent.	N, Per cent.	Organic matter, Per cent.
Point Firmin, Cal.	12.10	0.27	1.10	65.50
San Nicolas, Cal.	19.5	.50	1.01	52.40
	15.60	.27	1.63	56.20
	29.90	.35	.53	36.40
San Clement Island, Cal.	22.40	.41	.69	48.40
Average	19.90	0.36	.99	51.78

(6) There are no essential differences between the potash and nitrogen content of fronds and stipes.

(7) There are no essential differences in the potash and nitrogen content of old and young plants.[10] Further data on

[10] Some analyses reported recently show that very young nereocystis contained less than 20 per cent. potassium chloride, but nearly 5 per cent. nitrogen.

this point are, however, very desirable, as well as possible variations with the season.

Kelp as a Fertilizer.—That freshly-cut kelp has a high value as a manure is unquestionable, as the experience of hundreds of years in various parts of the world testifies. That such material could have any great importance in commerce, however, is impossible, for various reasons, more or less obvious, of which one is sufficient, namely, that it can not be made profitable to pay the freight on the large proportion of water in the kelp.

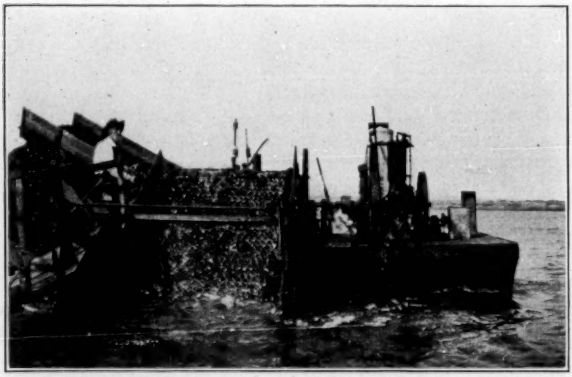
It appears that Balch gave considerable attention to this matter some years ago, and concluded that air-dried kelp, or material dried at ordinary oven temperatures, would not be suitable fertilizer. On the other hand, he concluded that kelp parched at temperatures of 200° C. to 240° C. underwent such changes that it could be satisfactorily used. This product he called "saline humus" and took out a patent (No. 771760, October 4, 1904) covering it. He described it as follows: "The material in this state,—*i.e.*, parched and ground,—can be marketed, *per se*, as a very cheap and efficient fertilizer, being rich in potassium salts and containing calcium and magnesium, both as phosphates and in combination with organic acids. The material also contains nitrogenous substances, which, as they decompose, yield ammonia and other compounds of nitrogen to the soil. It is also possible to mix this product with the various substances required by certain crops in the manufacture of a number of special fertilizers." Balch, however, clearly considered that the best utilization of kelp is to subject it to destructive distillation, recovering potassium chloride from the char, and obtaining at the same time various salable products.

As a "paper proposition" Balch's final suggestion leaves room for arguments as to details only. Practically, however, it appears altogether probable that the most desirable utilization of the giant kelps at this time is to dry them, and possibly to grind the dried product, depending on the condition of the product coming from the kiln. The material thus obtained is in an ideal mechanical condition for use as a fertilizer, either to be used directly or to be mixed with other materials.[11] Such samples

[11] For a comparison of the manurial value of dried kelp with ordinary potash salts see Skinner and Jackson, Circ. No. 76, Bureau of Soils, U. S. Dept. Agric., 1913.

have repeatedly been made in the laboratory, and have been tested with regard to its value as a fertilizer. The products so obtained have averaged above 15 per cent. potash (K_2O) and 2 per cent. nitrogen, the nereocystis sample running higher than those prepared from macrocystis. There can be no reasonable doubt that the material, if supplied in large enough lots and promptly to order, will find a ready market. The preparation of pure potassium chloride, iodine, gums, etc., may be practicable, and may ultimately prove more profitable. This is for the future to

FIG. 5.



End view of kelp harvester, Pacific Kelp Mulch Company, Los Angeles, Cal.

show. At present, however, and for the prompt establishment of a kelp business the preparation and sale of dried kelp offers by far the best opportunities.

Harvesting of Kelp.—Until recently the harvesting of the kelp on a sufficiently large scale to make it a commercial possibility appeared the chief stumbling-block. Numerous devices have been proposed and several tried out experimentally. By far the greater number of these proposed kelp cutters employed the well-known principle of the ordinary horse-drawn hay-mowing machine to be found on every farm. This principle is employed in a practicable machine now operating on the kelp groves near

Point Firmin, and the problem of cutting and harvesting the kelp can safely be said to be solved, although undoubtedly improvements and refinements of detail and technic are not only possible but surely to come with increasing experience. The device in actual practice consists of a flat decked barge. Over one end projects an endless belt device 16 feet wide and extending into the water to a depth of four feet or a little more. At the submerged end of this belt is a horizontal scythe blade, and at each end of the horizontal blade a perpendicular blade, each blade fitted with a gear device to give it a cutting motion

FIG. 6.

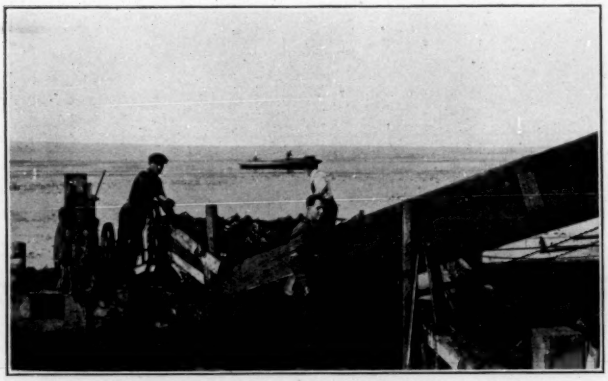
Kelp harvester. Hopper.

with a stroke of about four inches. The inboard end of the endless belt extends over a hopper, at the bottom of which is a set of revolving blades, of the type of an ordinary lawn mower. Below these revolving blades is the end of a belt conveyor on a pivoted frame and extending over the side of the barge. The whole device is mounted on appropriate frames and driven by a gasoline engine. In action an undecked towing barge is brought beside the cutter barge. A launch behind them pushes the barges through the kelp groves at a pace of about four miles per hour. The kelp as it is cut falls on the endless belt, is carried over the

hopper, through which it falls, is cut into six-inch lengths and conveyed over the side to the towing barge. Usually four men are employed—one on the launch, a second to watch the cutting and with a boat-hook ward off logs and similar floating materials sometimes entangled in the kelp. The third man attends to the loading and distribution of the kelp in the towing barge, and a fourth looks after the engine and running gear.

Cost of Harvesting Kelp.—This cutter has been in actual operation for upwards of a year, cutting kelp intermittently, but in the aggregate has harvested more than 2500 tons. Its opera-

FIG. 7.



Kelp harvester. Hopper and second conveyor.

tion is a very impressive and convincing sight, of which some idea can be obtained from the accompanying photographs.[12] To give the cost of harvesting green kelp is a difficult matter for several reasons. The existing data are limited. Definite figures have been obtained for only one locality and for only one equipment; and such definite data as the writer has were acquired in confidence. Disregarding earlier estimates, in the light of

[12] Acknowledgment is here made of the courtesy of Mr. George H. Ennis, of Los Angeles, Cal., in putting these photographs of a kelp harvester at the writer's disposal.

observations made this past spring, the writer estimated that green kelp could be harvested for 60 cents per ton, with an equipment consisting of: one cutter, cutting 500 tons per day of eight hours' actual cutting; two towing barges with 85 tons capacity each; two launches; and a total crew of six men. This price includes landing. Subsequently, figures were seen taken from actual practice which indicated that wet kelp from the Point Firmin groves could be landed at San Pedro or Long Beach at not to exceed 20 cents per ton. This figure would, of course, have to be modified for longer hauls or different equip-

FIG. 8.

Kelp falling from second conveyor into towing barge.

ments, but for the sake of arguments and tentative calculations it will probably be safe and conservative to estimate the cost of harvesting at 40 cents per ton of wet kelp. The cost of harvesting and marketing dried kelp as a fertilizer can now be estimated with a sufficiently fair approach to accuracy to determine at least the commercial possibilities. It is believed the following figures are all conservative, and the resultant is probably an underestimate. It will be convenient to make these estimates for a plant with a cutting barge, two towing barges, two launches, employing six men, and with a dryer and storage warehouse ashore employing three additional men.

Plant site	$10,000
Dryer, engine and mechanical equipment	4,000
Warehouse	5,000
Cutter and barge	4,000
Two towing barges at $4000 each	8,000
Two launches at $2000 each	4,000
Working capital	25,000
	$60,000

FIG. 9.

Kelp on towing barge.

Five hundred tons of green kelp is equivalent to 75 tons of dried kelp.

Harvesting	$200
Drying	45
Sacking	75
Overhead, interest and deterioration	50
	$370
Cost per ton of dried kelp	$4.93

Allowing 15 per cent. potash at 65 cents per unit and 2 per cent. nitrogen at $2.50 per unit, then the selling price of dried kelp per ton is $14.75. Net profit if sold at point of shipment should be $9.82. Assuming 200 working days a year on the average, a fair assumption on the Southern Californian coast,

there should be an annual production of 15,000 tons, worth approximately $147,000, a return of over 245 per cent. on the investment. If, however, there must be deducted freight and handling charges to the Atlantic seaboard, Hawaii, or Japan, to ship to Charleston or Baltimore *via* the Panama Canal, $5.50 per ton ought to be a fair estimate, which would leave $64,800, or 108 per cent. profit.

For the Puget Sound region it is to be doubted if a cutting season of over 100 days can be claimed. The cost of equipment would be about the same, but the other figures would have to be

FIG. 10.

Landing kelp at factory.

altered somewhat. It is altogether probable, however, that a return of at least 50 per cent. on the investment could be safely estimated.

While it is, of course, possible that a profitable business might be built up on a smaller scale than here assumed, and with a plant working intermittently, the prospects of a sound business would not be particularly alluring and would have no national importance. Comparatively little fertilizer of any kind is now used on the Pacific coast; and there seems to be a decided preference for potassium sulphate rather than the chloride. That the use of fertilizers will rapidly increase, and that with the increase the

value of dried ground kelp will be appreciated, is altogether probable; but for the present it is to the manufacturer of mixed fertilizers that one must look for the main market. The tonnage of fertilizers sold in the United States is steadily increasing, and at the same time the average grade of mixed fertilizers is steadily getting higher. The mixer at present makes less profit on the potash he puts in his goods, probably, than on any other constituent. Concession to him in price of his potash, and the fact that kelp is a carrier of nitrogen as well, would attract his attention, if he were assured of the ability to secure reasonably prompt delivery in large lots. For these reasons a fair margin of working capital, a storage capacity of several thousand tons, and a production of several hundred tons a week are considered necessary to insure a stable business.

Practicable Production of Potash from Kelp.—As to the number of units of the size here indicated, which could be profitably established, it is impossible to estimate with any approach to accuracy, and an opinion only can be offered. The consumption of potash in the United States at the present time, *expressed in terms of the chloride,* is approximately 841,000 tons. About 27 per cent. of the potash in the salts from Germany is in low-grade material whose importation would probably be much curtailed with the introduction of kelp potash on the Atlantic seaboard, although it is doubtful if the importation of high-grade goods would be much affected, barring the introduction of factors not now determining conditions. Taking everything into consideration, a growing market in this country, both East and West, and the probability of a trade with Hawaii, Japan, and the West Indies, it seems safe to estimate at least 300,000 tons of potassium chloride or about a million tons of dried kelp could be marketed per annum if it were now available. To produce this amount would require, according to the above estimates, 66 units with a capital investment of $4,000,000, and this in the face of a growing market.

Preparation of Pure Potassium Chloride.—The separation of pure potassium chloride from kelp is perfectly possible, so far as the theory and the technical features of the problem are concerned—at least on paper. Theoretically, it should be a very simple problem to add sufficient water to the kelp to dissolve the potassium chloride which would also be sufficient to dissolve all

the sodium chloride and to filter off the resultant solution. The residue when dried would contain 4 or 5 per cent. of nitrogen and should be worth $10 to $15 as a fertilizer and probably more as a cattle food, while the pure potassium chloride from the evaporated solution would be worth about $40 a ton. That is, the separation would increase the selling value of a ton of dried kelp from $14.75 to $25 or more, an attractive advance.

As a matter of fact, however, the freshly-cut kelp already contains far more than sufficient water to dissolve all the salts present. Unfortunately, moreover, the absence of fibre and the tissue structure of kelp is such that anything approaching a clean separation of salt and organic residue, by filtration, percolation, or even diffusion methods, seems impossible, or at least so difficult and consequently expensive as to be impracticable. On the other hand, a fair separation of the effloresced salts from the organic residue can be effected by agitating the dried kelp on a sieve.

The further separation of the potassium chloride from sodium chloride can be effected in several ways. The most satisfactory one would probably be to treat with water at two different temperatures, as, for instance, the boiling temperature of water, 100° C., and ordinary room temperature, say 25° C. The concentrations of the "constant solutions" for this salt pair at various temperatures have been determined by Precht and Witt.[13] For the sake of argument let it be assumed that the salt mixture contains 60 per cent. potassium chloride and 40 per cent. sodium chloride, an assumption apparently justified by laboratory experience. Further, using rounded figures as sufficiently accurate for the present purposes, assume the composition of the solution to be:

At 100° C.....	100 H_2O	35 KCl	26 NaCl
At 25° C.....	100 H_2O	16 KCl	29 NaCl

For the sake of simplicity the condition is imposed also that the mass of water remains or is kept constant. Commencing, then, with a thousand pounds of water at 25° and adding 725 pounds of the salt mixture, a brine will be formed, but at the same time there will be left a solid residue of 275 pounds of potassium chloride.

If, now, the solution be decanted or filtered from the residue,

[13] Ber., 14, 1667 (1881).

heated to 100° C., and 317 pounds of salt mixture added, 157 pounds solid sodium chloride will be formed.

Again decanting, cooling the brine to 25° C. and adding now 75 pounds of salt mixture, results in the formation of 235 pounds of solid potassium chloride. From this point on, each time the mother liquor is raised to 100° C. with the addition of 317 pounds of the salt mixture, 157 pounds of pure solid sodium chloride will be formed; and each time the mother liquor is cooled to 25° C. with the addition of 75 pounds of salt mixture, 235 pounds of pure solid potassium chloride is obtained. The two processes form a cycle involving: (1) two decantrations or filtrations, (2) one lifting of a 30 per cent. (approximately) brine or two pumpings, one in each direction, and (3) the heating of a 30 per cent. brine to 100° C., besides (4) several shovellings of salt mixture and divers minor mechanical operations.

Comparative Values of Sifted and Unsifted Kelp.—If it be assumed that in shaking the effloresced salt from the kelp the organic residue remaining is 50 per cent. of the total and that 20 per cent. as sodium chloride and 30 per cent. as potassium chloride is in the salt mix, then it will require three and one-third tons of dry kelp to produce one ton of potassium chloride. At $3.93 per ton for the dry kelp a ton of potassium would cost in the raw material $13.10. The cost of the heating and pumping operations, in the cycle above outlined, would cost less than 5 cents per ton of brine, or about 50 cents a ton of potassium chloride. Allowing, then, for one ton of potassium chloride:

Raw material	$13.10
Heating and pumping	.50
Bagging	1.00
Labor	.20
Overhead, depreciation, etc.	1.00
	$15.80
Cost	$15.80
Selling price	40.00
Profit	$24.20

The organic residue, amounting to one and two-third tons, with a nitrogen content of 4 per cent., would be worth $10.65

(at $2.50 per unit for nitrogen). Allowing nothing for the sodium chloride as balancing the cost of the sifting, then three and one-third tons of dry kelp with the potassium chloride sifted out would bring $34.87, or one ton of dry kelp would bring, after sifting and recrystallization, $10.46, against $9.82 when not further treated. In other words, there would be apparent gain if the products were sold at the point of manufacture. But it is to be noted that there is a saving of 20 per cent. in freight, due to the elimination of sodium chloride, so that the profits at Baltimore or Charleston would appear to be, respectively, $4.32 and $6.06 in favor of the sifted and recrystallized product. If the organic residue were sold on the Pacific coast as a cattle food and the potassium chloride alone shipped to the Atlantic seaboard, the margin would become even greater, and the operations of sifting and recrystallizing would show sufficient advantage to justify the kelp being handled in that way.

But the separation of organic residue from the salt, so far as laboratory experience goes, is very far from being as complete as assumed in the foregoing calculations, and there is as yet no factory experience involving the handling of large masses of dried kelp from which even an intelligent guess can be made. At present it would appear to be much sounder business policy to depend on the marketing of the dried kelp without further treatment, unless, indeed, it be found desirable to pass it through a grinder, a comparatively inexpensive operation with such material. On the other hand, it is to be noted that the procedure of crystallizing at alternate temperatures, first the sodium chloride and then the potassium chloride, would finally concentrate a high percentage of potassium iodide in the mother liquor, so high that it could be easily recovered and add to the value of the process.

Existing Kelp Companies.—Since attention has been directed to the commercial possibilities of giant kelps there have been a number of companies proposed for their exploitation. Some have been perfectly legitimate, straightforward enterprises, others merely stock-jobbing propositions, and some, the most objectionable "wild-cat" schemes. Of the proposed companies now before the public, four have given tangible evidences of good faith by actual investment in equipment. The Pacific Products

Company of San Pedro, Cal., with a capital of $100,000, has a factory on the open coast opposite the great kelp grove outside Firmin Point. This position assures a short haul of the harvested kelp, but is open to the objection of an anchorage of doubtful safety in stormy weather. The company claims that a breakwater now building will meet this objection. It is proposed to pass the wet kelp through rollers, char it, lixiviate the char, and evaporate the lixiviate in shallow pans over the charring oven. The purpose is to recover by crystallization a high-grade potassium chloride, as the raw material for the preparation of various pure potassium salts. The plans appear unnecessarily complicated and expensive for the production of potassium chloride alone. Samples of various grades of potassium chloride, charcoal, and iodine prepared by this company appear to be very satisfactory and merchantable products. The Pacific Kelp Mulch Company has offices in the Union Oil Building, Los Angeles, Cal., and a factory site at San Pedro. The site has a convenient water front, is practically beside a railroad spur, and contains a good deal of apparatus and paraphernalia used in experimental work on the production of various kelp products. This company has a cutter mounted on a decked barge, two open towing barges of 40 tons and 85 tons capacity of a special design to avoid straining in towing through a swell or heavy water, and a powerful launch. This company is reported to be building a larger and much improved cutter which will require but two men to operate; and they are building new 85-ton towing barges. Up to the present this company has been cutting and selling the wet kelp directly, last year marketing about 2500 tons. Some objections have been urged against this product, mainly as regards its price, because it has a low content of "plant foods." It is difficult, moreover, to send samples to the laboratory without loss of water *en route* sufficient to materially raise the content of potassium; and, finally, because it is held by some authorities that California soils are normally sufficiently supplied with potassium. Inquiries of several purchasers and users of "kelp mulch" have brought testimony favorable to the kelp. Moreover, as the accompanying table shows, the material compares quite favorably with ordinary stable manure and street sweepings, and should therefore command a commensurate price.

TABLE VI.

COMPARISON OF THE COMPOSITION OF WET KELP WITH OTHER MANURIAL PRODUCTS.

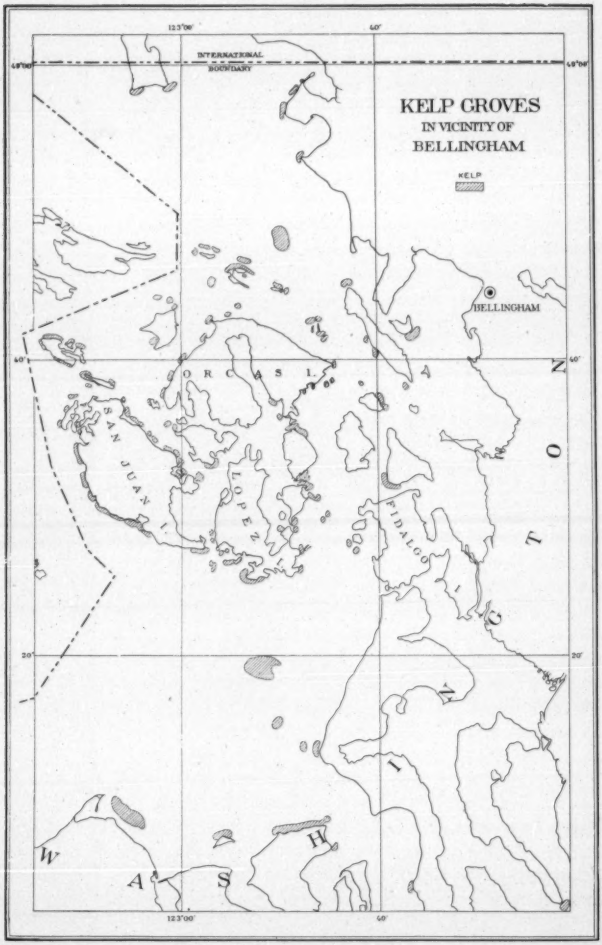
	Moisture, Per cent.	Nitrogen, Per cent.	Potash, Per cent.	Phosphoric acid, Per cent.
Horse manure[1]				
Solid fresh excrement	.....	0.44	0.35	0.17
Fresh urine	.....	1.55	1.50	....
Stable manure[1]	73.27	.50	.60	.30
Green alfalfa[1]	75.30	.72	.45	.15
Cowpeas[1]	78.81	.27	.31	.98
Garbage-tankage[2]	.....	.70	.30	.60
Street sweepings, Washington, D. C.[3]	.....	.86	.55	.55
Wet kelp	85.00	.30	2.50	.20

[1] From Soils, by S. W. Fletcher.
[2] From Fertilizers and Crops, by L. L. Van Slyke.
[3] From Analyses, by J. G. Smith, Bureau of Soils.

The Pacific Kelp Mulch Company is now preparing dried kelp near Ensenitas, on the Mexican coast, cutting under the Bernstein concession, and is understood to be working on a plan for artificially drying the kelp at its San Pedros plant, and expects to put the material on the market at an early date. The company is capitalized nominally at $500,000, but has issued about two-fifths of its stock. Its promoters have invested many thousands of dollars in experimental work, an investment which appears to be in rapid recovery. The company must be recognized as the first organization to actually harvest kelp on a commercial scale, to market its product on a profitable basis, and to demonstrate, practically, that a real business opportunity exists in the production of a "kelp fertilizer."

The American Potash Company, with offices in the Los Angeles Investment Building, Los Angeles, Cal., has a most desirably located site of about 12 acres on the water front of Long Beach, Cal. This company possesses two powerful boats, as well as several smaller boats. It has absorbed the Coronado Chemical Company, formerly of San Diego, with a plant at Cardiff, and the Ocean Products Company, with a plant at Half Moon Bay, near San Francisco. The machinery and apparatus at these former plants have been moved to the Long Beach site. Experimentation on cutting kelp had been carried on by one of these companies with, it is claimed, successful results; but it is

FIG. 11.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60'

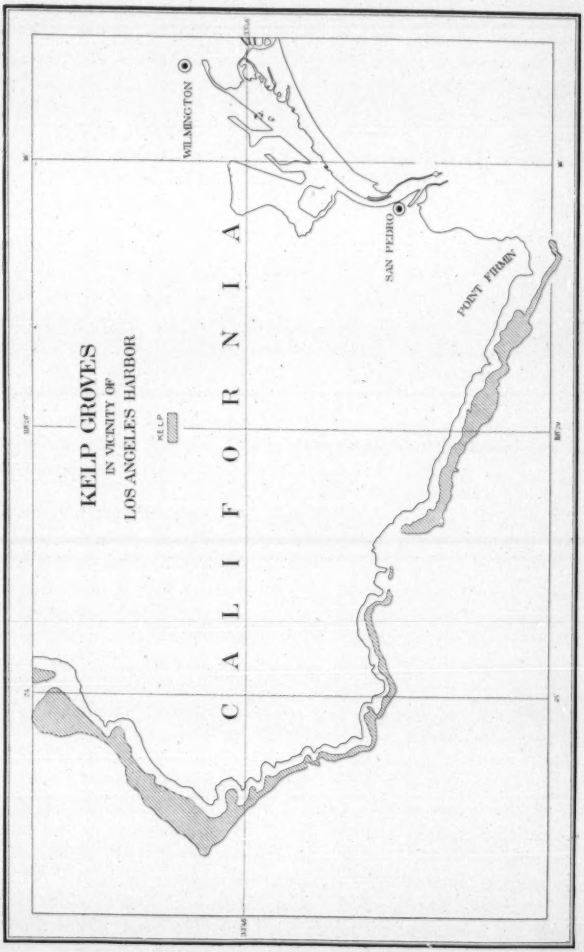

KELP GROVES
IN VICINITY OF
LOS ANGELES HARBOR
KELP
CALIFORNIA
WILMINGTON
SAN PEDRO
POINT FIRMIN

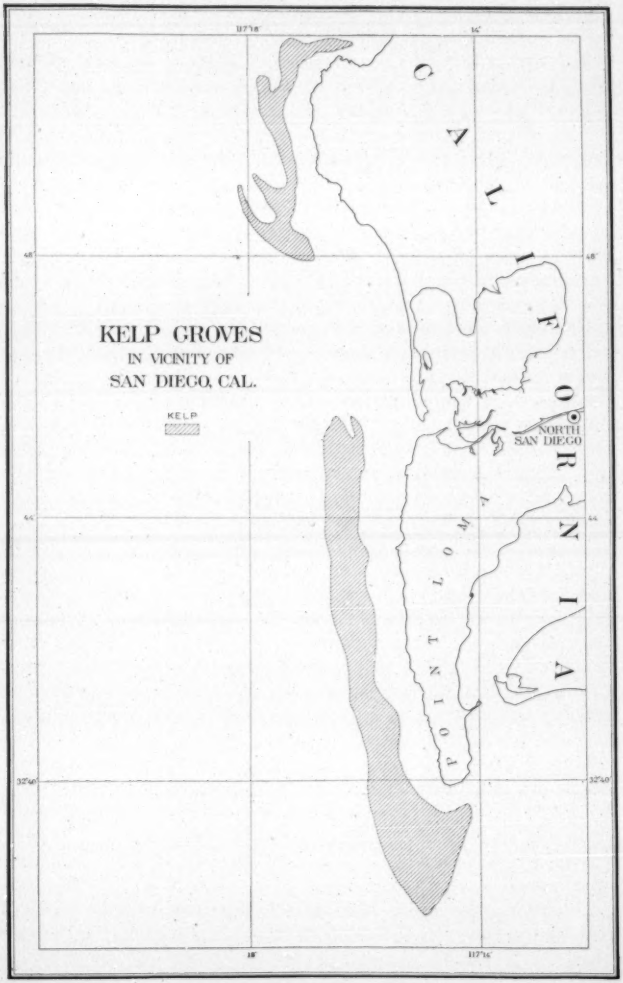
FIG. 12.

probable that this company, like all those now existing on the coast, will actually use a model more or less similar to that of the Pacific Kelp Mulch Company, illustrated in the accompanying photographs. This company announces as a result of experimentation at Half Moon Bay that it expects to produce creosote, lacquers, and various other products, potassium salts included. It is understood, however, that its main production at first will be dried kelp for fertilizer, whose profitable marketing is far better assured than the products above cited or the others described in the preliminary literature of this company. By an ingenious shaking device this company announces that it will sift the effloresced potash salts from the organic residue, thus producing a higher grade potassium chloride on the one hand, and a highly nitrogenous product on the other, the latter being susceptible of higher concentration by washing out the sodium chloride with cold water. The company has a nominal capital of $1,500,000, appears to have sound financial backing, and to be in a position to obtain ample working capital for initial operations, securing it by a trust on the property above cited. The marketing of dried kelp and possibly other products this summer is promised.

The Pacific Products Company of Seattle, Wash., is preparing to operate on a different plan. It expects to harvest kelp on Puget Sound, where, from the nature of the plant and the weather conditions of the region, there must be a shorter season, confined to definite months. This company expects to produce oil and scrap from salmon cannery wastes. It has produced a very fine grade of oil from the livers of dog-fish, which are becoming very common in those waters, the rest of the carcasses being treated in the usual way for fish oil and scrap. Practically the same equipment will be utilized for handling fish scrap and kelp. This company has a capital stock of $125,000. It is reported that 95 per cent. of the stock is owned by the directors of the company, about a fifth of the stock has been paid in for operation expenses, and that there are no bonds issued, nor outstanding indebtedness. It is also reported that the company will be prepared to market its products this summer or fall.

Desirable Locations for Manufacturing Plants.—Although there are a number of points on the Pacific coast where plants could be located for the profitable production of potash from

FIG. 13.


KELP GROVES
IN VICINITY OF
SAN DIEGO, CAL.
KELP
CALIFORNIA
NORTH
SAN DIEGO
POINT LOMA
117°18'
16'
48'
44'
32°40'
18'
117°16'

kelp, inspection of the working maps of the kelp groves shows four points to merit special consideration because of the proximity of abundant supplies of kelp, together with satisfactory labor and transportation facilities. These points are: Puget Sound, in the neighborhood of Bellingham or Anacortes, and Santa Barbara, Los Angeles, and San Diego, Cal.

As pointed out above, the harvest season in the Puget Sound region is short, and a kelp business will most likely command success if carried on in coöperation with the utilization of cannery wastes or other fish oil and scrap operations. The general character of the kelp groves is indicated by the accompanying map (Fig. 11), showing the distribution in the neighborhood of Bellingham. The Puget Sound kelp should yield about 390,000 tons per annum of wet kelp, or enough to justify the existence in that neighborhood of 4 units of the capacity considered in the foregoing pages. As, however, the season in the Puget Sound region is probably not over half the length of the season on the southern coast, it might prove advantageous to provide 7 units, to be employed the rest of the time in handling scrap. Labor conditions in this region are fair and transportation facilities excellent. Furthermore, supplies of kelp or kelp ash from Alaska may become an added factor of importance for plants in this region.

Santa Barbara has before it a large grove of macrocystis through which a ship channel is maintained, dividing the grove into approximately equal parts. Labor conditions are probably fair and there are possible good railroad facilities. Facilities for shipment by water are not very favorable. The harbor is made practically by the kelp grove forming a natural breakwater, and the depth to landing is too shallow for large vessels and the landing facilities are meagre. The area of the Santa Barbara kelp grove is approximately 3.9 square nautical miles, and on one cutting to a depth of 4 feet would yield over 320,000 tons of wet kelp. As two cuttings a year could probably be made, over 600,000 tons should be annually available, enough to justify the existence of 6 units of the capacity described above. Other groves accessible from this point would justify an even larger installation.

From Point Firmin to Malaga Cove are two large kelp groves readily accessible from San Pedro and Long Beach, the harbors

of Los Angeles. The position and extent of these groves is indicated in the accompanying map (Fig. 12). Labor facilities are here relatively good, and both railroad and water transportation facilities are quite satisfactory. One of these groves has an area of about 0.76 square nautical mile and is estimated to be able to produce on one cutting to a depth of 4 feet about 62,500 tons of wet kelp, or 125,000 tons on two cuttings. The large grove contains about 1.6 square nautical miles and should yield 131,500 tons of wet kelp on one cutting, or over 260,000 tons on two cuttings. Other accessible groves in the neighborhood augment considerably this estimated production. There is enough kelp in this neighborhood to justify the installation of 4 units of the capacity discussed above. The three companies already installed in this neighborhood should, before long, practically monopolize the kelp production in the immediate vicinity. Outside the harbor of San Diego, between Point Loma and La Jolla, as indicated on the accompanying map (Fig. 13), lie two large groves of very heavy kelp. The combined area of these two groves is about 7.7 square nautical miles, and it is estimated that they should produce 633,000 tons of wet kelp on one cutting to a depth of 4 feet, or 1,265,000 tons on two cuttings. This tonnage alone would justify 12 or 13 units, but, considering the position of San Diego with respect to the numerous large groves on the Mexican coast, 15, or even perhaps 20, units could be surely supplied with raw material. Labor facilities at San Diego are fair, railroad facilities are good and improving, and facilities for transportation by water excellent. Plant sites which are now cheap are likely, however, to be much more costly in the near future. All things considered, San Diego appears to offer unusual advantages for a large and profitable production of "potash from kelp."

Purification and Concentration of Radium Barium Chlorides. E. EBLER and W. BENDER. (*Ber.*, xlvi, 1571.)—When hydrochloric acid gas is led into mixtures of barium and radium chlorides till it produces precipitation, the first fractions precipitated are richer in radium than the later ones, and practically the whole of the radium is precipitated before 75 per cent. of the barium is. This method of enrichment is far preferable to that of fractional precipitation as sulphate from every point of view.

"Bungo" Sulphur. ANON. (*Oil, Paint and Drug Rep.*, May 12, 1913.)—In Bungo province, Japan, there are many geyser-like craters which emit sulphurous fumes intermittently when volcanic activity induces action. During their inactive periods the Japanese have placed pipes in the ground and in the crevices about the craters of these so-called geysers in such a position that when the active period commences the fumes are collected in these pipes and conducted into hermetically tight reservoirs, from which the condensed sulphur flows down the mountain side in long, light conduits, where it solidifies, and from which it is taken, broken into irregular pieces, sacked and transported by coolies to the markets and sold under the name of Bungo sulphur.

Solubility of Sulphur in Rubber. H. LOEWEN. (*Gummi Zeit.*, xvii, 1301.)—The following experimental evidence supports the view that one of the phenomena of vulcanization consists of the solution of sulphur in the rubber. A small quantity of a mixture of Para rubber with 10 per cent. of sulphur was pressed between a microscope slide and a cover-glass, warmed to about 80° C., and heated in a hot-air oven at 130°–140° C. The slide was examined at intervals under the microscope. After a very short heating the sulphur was found to be distributed through the mass in globules of various sizes; when the heating had continued for 20 to 30 minutes, the mass appeared perfectly clear and transparent immediately after removal from the oven, but on cooling became cloudy to the naked eye. This turbidity is due to the separation of small globules of super-cooled liquid sulphur, which crystallize on standing. That this is a case of ordinary molecular solution, and not of colloidal solution, is shown by several experimental results, two of which are quoted: (1) If the slide be heated for increasing length of time until the point is reached when the preparation just remains clear on first cooling down, the free sulphur separates from the cooled mass in the crystalline form, and not in liquid drops which crystallize afterwards. The solubility of sulphur is higher in vulcanized than in unvulcanized rubber, and this agrees with the fact that highly vulcanized rubber, ebonite, does not "sulphur up," although containing high percentages of free sulphur. (2) If a fragment of rubber without sulphur be pressed between slide and cover-glass, and molten sulphur be applied round the edges of the glass so as to be drawn into contact with the rubber by capillary action, and the preparation be then heated in the oven for about 45 minutes, the sulphur diffuses into the rubber for a considerable distance in a manner characteristic of true solution. In view of these results it is considered that adsorption plays no part in the process of vulcanization, the three stages of which are fusion of the sulphur, solution of the sulphur in the rubber, and the chemical combination of sulphur with rubber.

THE USE OF THE SYNCHRONOUS COMMUTATOR IN ALTERNATING CURRENT MEASUREMENTS.*

BY

FREDERICK BEDELL, Ph.D.,

Professor of Applied Electricity in Cornell University.

ALTHOUGH the commutator or rectifier has been used in a number of laboratories for making certain alternating current measurements, and although some of its uses for specific purposes have been described or referred to by various writers whose names are given later, the uses to which it can be put do not seem to be widely known, nor has there been any general discussion of the subject. So wide is its scope—giving a direct method for measuring alternating flux, for measuring maximum voltage in insulation and other testing, superseding, in a way, the older methods of instantaneous contact for determining alternating current wave form, and making available direct current galvanometers and other instruments for various kinds of alternating current measurements—that it is believed a better knowledge of the possibilities of the rectifying or integrating commutator will lead to its more common use in our testing and educational laboratories.

The underlying principles of the methods here described are not new; some features in their development and application, however, are now described for the first time.

The mechanical structure of the apparatus may be varied; any form of switch can be used that reverses the circuit connections twice each cycle. A simple arrangement of apparatus for accomplishing this is as follows:

A commutator is driven in synchronism with the alternating current upon which tests are to be made, being direct-connected to a small synchronous motor or mounted on the shaft of the supply generator. The commutator has as many segments as the machine upon which it is mounted has poles. Alternate segments are connected together, thus forming two sets of segments that are connected, respectively, to two slip rings upon

* Communicated by the author.

which bear two brushes, $b\ b'$, which can be connected to a source of alternating current to be measured. Bearing upon the commutator, and accurately set so as to be separated from each other by a distance of one commutator segment, are two brushes $B\ B'$ from which can be derived rectified current that can be read by a direct current measuring instrument. These brushes are so mounted that, without changing the distance between them, they can be shifted and their position read upon a scale graduated in degrees. When the brushes are given such a position that commutation takes place at the zero point of the alternating current wave, the alternating current becomes completely rectified so as to be unidirectional.

It will be noted that each degree of mechanical shifting of the brushes corresponds to one degree of electrical phase when the driving machine has two poles, to two degrees of electrical phase when the driving machine has four poles, and so on. A tangent screw or some fine adjustment for setting the brushes should be provided. It is desirable that means be provided for conveniently shifting the brushes by successive equal steps of say 5 degrees or 10 degrees, and also for shifting them quickly through 90 degrees of electrical phase. A form of apparatus used by the writer is shown in Fig. 1.

It will be seen that any commutator of this general type can be used only on alternating currents that change sign every half cycle and have similar positive and negative waves; it can be used on all usual alternating current circuits, but not in the unusual case in which even* harmonics are present. This limitation does not apply to the condenser discharge method for the determination of wave form of voltage and current (Part VII), for this method can be applied to any pulsating wave, unidirectional as well as alternating, that varies periodically; that is, there may be present even as well as odd harmonics and also a constant term.

Thin metallic brushes should be used, that can be set accurately without bridging across adjacent commutator segments; the resistance of brushes and contacts should be as low and

* When both odd and even harmonics are present, methods IV, V, and VI can be used to determine the wave form of the sum of the odd harmonics only. The wave form of the sum of the even harmonics can be determined by a separate commutator with twice as many segments.

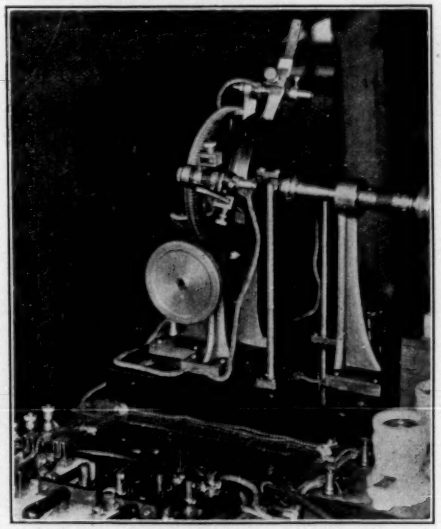
uniform as possible, for in some of the methods these conditions contribute to the precision of the results. The commutator and galvanometer circuit should be well insulated from the motor and its circuits, particularly from the direct current field circuit.

The following uses of the commutator will be discussed:

I. Determination of average value of alternating electromotive force and current.

II. Use as zero instrument.

FIG. 1.



III. Determination of form factor of alternating current or voltage.

IV. Determination of wave form and maximum value of alternating magnetic flux.

The determination of wave forms and maximum values of alternating currents and electromotive forces:

V. By the air transformer method.

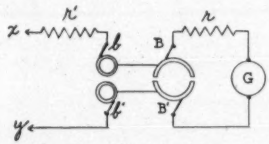
VI. By the condenser current method.
VII. By the condenser discharge method.
VIII. The determination of phase difference.
IX. General and historical.

In preparing this paper it has been the writer's aim to describe the essential elements of the several methods. Modifications may be made in arrangement of apparatus, in procedure, and in methods of calibration to suit the requirements of particular cases.

I. DETERMINATION OF AVERAGE VALUE OF ALTERNATING ELECTROMOTIVE FORCE OR CURRENT.

Electromotive Force.—To determine the average value of the alternating electromotive force between the line terminals xy, the line is connected through the rectifying commu-

FIG. 2.



Arrangement of commutator and galvanometer.

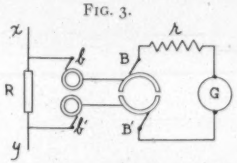
tator to a D'Arsonval galvanometer G,—which in this case may be a Weston direct current voltmeter,—as shown in Fig. 2. One pair of brushes is connected to the line; the other pair to the galvanometer. A non-inductive resistance or multiplier r is connected in series on the galvanometer side of the commutator; when a voltmeter is used this resistance may be contained as part of the instrument. In comparison with r, the resistance of the brush contact and the inductance of the galvanometer will usually be insignificant. When the line voltage is higher than can be commutated without danger of sparking or short-circuiting,—that is, in practically all voltage measurements,—additional series resistance r' should be placed on the line side of the commutator, or the line voltage should be stepped down by a transformer. The procedure to be followed in taking readings is described below.

To obtain the actual voltage across xy, when resistances r

and r' are used, the readings of the galvanometer or voltmeter should be multiplied by a proper constant; or the instrument should be calibrated on direct current * with these resistances in circuit by comparison with a standard direct current voltmeter.

Current.—To determine the average value of an alternating current, insert in series with the circuit a low non-inductive resistance R (commonly called a shunt) and connect the terminals of R through the commutator to the galvanometer G, which may be a millivoltmeter, as shown in Fig. 3. Connections should be well made so that the resistance remains as constant as possible. A resistance r in the galvanometer circuit will reduce any error due to inductance of the galvanometer or to variable resistance of brush contact, but for the same sensi-

FIG. 3.



Connection for current measurement.

tiveness will require a correspondingly greater resistance and voltage drop in R, which may be a disadvantage.

The resistance r is better placed on the galvanometer side rather than the line side of the commutator in this case (and in similar low potential cases, as, for example, the air transformer method for determining current), so that any static electricity that might be generated in the commutator would flow through R rather than through G,—an effect usually negligible, however.

The instrument may be calibrated on direct current by comparing its reading with a standard ammeter connected in series

* If the commutator is running during the calibration on direct current, G will not read unless placed on the line side of the commutator in series with r'. If a suppressor (described later) is used instead of a commutator, the suppressor may be running and G will read on direct as well as on alternating current without this transfer. The use of a suppressor has this advantage.

Calibration can be made upon an alternating current circuit of known form factor f, the average voltage being equal to the effective voltage measured by a standard alternating current voltmeter divided by f.

with the line. If the commutator is running (as it should be when the highest accuracy is desired), G must be transferred to the other side of the commutator, being in series with the connection between R and the commutator (see preceding note).

For measuring very small currents, the shunt R can be omitted, so that all the current is commutated and passes through the galvanometer.

Procedure.—In measuring alternating current or voltage by this method, commutation should take place at the zero point of the alternating wave. The deflection of G will then be a maximum and will accurately indicate the average value of current or voltage. There are several methods by which the proper reading can be obtained.

(1) *Maximum Deflection Method.*—The brushes are shifted until the deflection of G is a maximum, when a reading is taken. This method is correct in principle, but it is not easy to quickly set for a maximum.

(1a) *Maximum Deflection Method with Non-Synchronous Commutator.*—If the commutator is driven slightly off from synchronism, as through a series of gears by a synchronous motor or directly by an induction motor, no shifting of the brushes is necessary. The deflection of G has beats; a reading is taken when the deflection is a maximum. This method is correct in principle; readings cannot be taken with great accuracy.

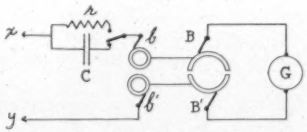
(2) *Special Contactor Method.*—A second galvanometer, G, in an independent auxiliary circuit, is connected in circuit at a definite instant in each revolution by a revolving contact-making point P touching an adjustable brush B'', as in the well-known instantaneous contact methods. P is in line with the insulation between commutator segments; B'' is in line with one of the brushes BB' and is carried by the same rocker arm.

The brushes are shifted until G' reads zero, thus insuring commutation at the zero point of the alternating wave; a reading of G is then taken. A condenser in parallel with the second galvanometer G' will increase its sensitiveness.

This method is correct in principle and gives rapid and accurate readings. It requires, however, a special contactor as described. A single galvanometer with suitable switches can be used, but the method is far more convenient with two instruments.

(3) *Condenser Method for Commutating at Zero.*—The resistance r is placed on the line side of the commutator as in Fig. 4. The resistance of the galvanometer circuit should be small. A switch is arranged so that a condenser C may be connected in circuit in place of the resistance r. With C in circuit, the brushes are moved until G reads zero, thus locating the zero of the wave as in the condenser current method (Part VI) discussed later; the resistance r is then substituted for C and a reading of G is taken.

FIG. 4.



Condenser method for commutating at zero.

This method insures correct commutation at zero for all wave forms, requires no special apparatus—other than a condenser—and is simple in operation.

(4) *Quadrature Shift of Brushes.*—The brushes are moved until G reads zero, and are then shifted 90 degrees of phase, or one-quarter cycle; readings of G are taken.

This method is positive in taking readings, but may introduce error with irregular shaped waves, for commutation is not necessarily at the zero point, as it should be, being 90 degrees from a median line dividing the wave area in half. Shifting the brushes 90 degrees may be a tedious process, unless the apparatus is specially constructed with this in view.

(5) *Quadrature Shift of Synchronous Motor.*—The quadrature shift may be made not by shifting the brushes but by throwing the synchronous driving motor from one phase to the other of a two-phase supply circuit. This introduces the same error as is introduced by shifting the brushes, and may introduce additional error if the two phases of the supply circuit are not in exact quadrature.

Uses.—The commutator method for measuring alternating currents makes possible the accurate measurement of very small alternating quantities—milliamperes, millivolts, and smaller—which cannot be measured by the usual instruments or methods.

The average value of an alternating current or electromotive force gives data for determining *form factor*, discussed in a following section.

As the average value obtained by the commutator method is the algebraic average for a half cycle, the average value and form factor thus obtained lose significance when applied to any voltage or current that is not continuously of one sign for half a cycle. (This limitation does not apply to any of the methods for determining wave form described in the subsequent sections.)

II. USE AS ZERO INSTRUMENT.

By means of the rectifying commutator, arranged as described in Part I, any D'Arsonval galvanometer or other direct current instrument can be used as a zero instrument on alternating current with the same sensitiveness as on direct current. It thus becomes a most satisfactory instrument for potentiometer measurement or bridge measurement on alternating current circuits. With the synchronous commutator, the brushes are first set for a maximum galvanometer reading; circuit conditions are then changed until the galvanometer reads zero or a minimum. With a non-synchronous commutator the shifting of the brushes becomes unnecessary.

In balancing a known and an unknown quantity in potentiometer measurement so as to obtain a zero reading it should be kept in mind that the commutator method balances the *average* values of the two quantities, whereas a dynamometer balances *effective* values and a vibration galvanometer balances the values of the *fundamental* or other harmonic to which it is tuned. In some cases these differences may become significant. (The above statement in regard to the dynamometer refers to its use in the usual manner, and not to its use with separate excitation, in which case the wave form of the excitation should also be considered.)

III. DETERMINATION OF FORM FACTOR OF ALTERNATING CURRENT OR VOLTAGE.

The form factor, f, of an alternating current or voltage is found by dividing its effective value by its average value.

The effective value may be found by a dynamometer or A.C. instrument D, connected across the line. The average value may

be found, as in Part I, by a commutator and galvanometer or D.C. instrument G, which is read when a maximum and has previously been calibrated in terms of D.

As D will read on D.C. as well as on A.C., a simpler procedure is to connect D on the same side of the commutator as G, the two instruments being in parallel. Any resistances r' or r in series with the two instruments, as in Fig. 2, may be of unknown value. Simultaneous readings, d and g, of the two instruments are first taken on alternating current with the commutator running, the brushes being set so that g is a maximum. Readings d' and g' are then taken on direct current with the commutator stationary. No further calibration is necessary. The form factor is then $f = d\ g' \div d'\ g$. For greatest accuracy the readings on direct and on alternating current should be on about the same parts of the scales.

Form factor may be found by first determining the instantaneous values of the wave by one of the methods subsequently described. The effective value is the square root of the average of the squares of equidistant instantaneous values for one-half cycle. Or, if the instantaneous values are plotted as a polar curve, the effective value is the square root of $2/\pi$ times the area of the polar curve for half a cycle, as found by a planimeter. The average value may be found by averaging the instantaneous value; or it may be found from the area of the curve plotted with rectangular coördinates.

As an illustration of the significance of form factor, the maximum value of the flux in a transformer (upon which depend the core losses) is directly proportional to the average value of the voltage, which in turn is equal to the effective measured voltage divided by the form factor.

IV. DETERMINATION OF WAVE FORM AND MAXIMUM VALUE OF ALTERNATING MAGNETIC FLUX.

Wave Form of Flux.—From the terminals xy of a coil (preferably a secondary coil) embracing the flux to be measured, connections are made through the synchronous commutator and suitable resistances, as in Fig. 2, to the galvanometer G, which in this case may advantageously be a Weston voltmeter. Let V be the reading of the galvanometer or voltmeter calibrated, with the commutator running, to read volts at

the terminals xy. Let S be the number of turns in the coil, and let n be the frequency of the circuit.

If readings of V are taken for successive positions of the commutator brushes, the instantaneous value of the flux corresponding to any reading is

$$\varphi = \frac{V \times 10^8}{4nS}.$$

The wave form of flux is thus determined.

The only other method for obtaining a wave form of flux is to derive it by integration from the wave form of voltage, and this may be done as a check. The usual procedure * is to integrate by means of a planimeter, which is somewhat laborious.

Maximum Flux.—The maximum value of flux is determined by the maximum reading of V, which is the average voltage, or E_{av}; that is,

$$\varphi_{max.} = \frac{V_{max.} \times 10^8}{4nS} = \frac{E_{av.} \times 10^8}{4nS}.$$

It is seen that the maximum flux in a magnetic circuit, as for example in a transformer, depends upon the average value of the voltage, rather than upon the maximum or effective value. When only maximum values of flux are desired, a non-synchronous commutator can be used; or any of the procedures can be followed that were described in Part I for determining average voltages.

Proof.—These relations may be proved as follows: We have the fundamental relation $d\varphi = -e\,dt \div S$. During any time interval of half a period T,—that is, from any time $t = t_1$ to $t = t_1 + \frac{T}{2}$,—the flux changes from $+\varphi$ to $-\varphi$, the negative and positive waves being similar. Integrating, therefore, for half of a period, we have

$$\int_{+\phi}^{-\phi} d\varphi = -\frac{1}{S}\int_{t_1}^{t_1+\frac{T}{2}} e\,dt.$$

* A simpler procedure than integrating by a planimeter is as follows: Let $y_1, y_2, y_3, \ldots y_n$, be successive equidistant ordinates of the electromotive force wave, beginning arbitrarily with any initial ordinate y_1; these ordinates may or may not be actually plotted. The corresponding ordinates for the flux wave are proportional to y_1, $(y_1 + y_2)$, $(y_1 + y_2 + y_3)$, $\ldots$ $(y_1 + y_2 + \ldots y_n)$, in each case being proportional to the algebraic sum of any particular ordinate y_n and all preceding ordinates.

But the reading of the voltmeter is

$$V = \frac{2}{T}\int_{t_1}^{t_1+\frac{T}{2}} e\,dt,$$

this being the average ordinate of the voltage curve during a half cycle subsequent to any time t_1. Hence we may write

$$-2\varphi = -\frac{TV}{2S}.$$

Substituting $1/n$ for T, and introducing 10^8 when V is in volts, we have

$$\varphi = \frac{V \times 10^8}{4nS},$$

which is the value of the flux at the time t_1 and (with change of sign) at the time $t_1 + \frac{T}{2}$. The reading of the voltmeter depends solely upon the value of the flux at the time of commutation, and is independent of any intermediate values.

V. AIR TRANSFORMER METHOD FOR THE DETERMINATION OF WAVE FORM AND MAXIMUM VALUE OF ALTERNATING CURRENT AND ELECTROMOTIVE FORCE.

Wave Form of Current.—The primary of an air core transformer is connected in series in the circuit in which the instantaneous value of the current i_1 is to be determined. The secondary of the transformer is connected, through the synchronous commutator, to the galvanometer or voltmeter. The resistance of the secondary and galvanometer circuit should be high, so that the effect of self-inductance in this circuit is small. Letting M be the mutual inductance of the transformer, we have the secondary voltage

$$e_2 = Ri_2 = M\frac{di_1}{dt}, \text{ or}$$

$$di_1 = e_2 dt \div M.$$

Hence, by a proof similar to that previously given (Part IV), the instantaneous value of the current corresponding to any reading V (in volts) of the galvanometer or voltmeter is

$$i_1 = \frac{V}{4nM},$$

where n is the frequency of the circuit.

As the commutator brushes are shifted into successive positions, the reading V multiplied by a proper constant will thus give the instantaneous value of current.

When M is not known, the proper constant can be found by comparing the effective value of the current, as measured by a standard ammeter, with the effective value found by taking the square root of the mean square of the instantaneous values, or by taking the square root of $2/\pi$ times the area of a curve plotted in polar coördinates, for half a cycle. Other methods of calibration may suggest themselves.

By varying the relative positions of the primary and secondary windings, the value of M and so the sensibility of the galvanometer can be varied at will.

In determining the wave form of current of a high potential circuit this method has the advantage that the air transformer insulates the testing apparatus from the line circuit.

Wave Form of Electromotive Force.—The primary of the air transformer, in series with a high resistance R_1, is connected across the circuit under test. The commutator and galvanometer or voltmeter are connected to the secondary as before. The fall in potential due to R_1 must be large compared with the inductive electromotive force in the transformer primary, so that the primary current at any instant will be proportional to the line voltage at that instant. The proper constant can be found by calculation or by calibration as described above. If the maximum voltage of some circuit is known, this value may be compared with the maximum reading of the galvanometer.

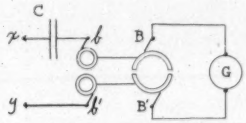
The air transformer method gives more difficulty in calibration than the condenser current or condenser discharge method described later, and is subject to error if the circuit constants are not suitably chosen. It seems to have a wider range of usefulness in determining wave form of current than of voltage. For very high voltages it is not so well suited as the condenser current method; nor is it so well suited for very low voltages on account of the necessarily high resistance R_1.

Maximum Values.—The maximum value of the current or the voltage is determined by the maximum reading of the instrument as the brush position is varied. When maximum values only are desired, a non-synchronous commutator can be employed or various procedures can be followed as given in Part I.

VI. CONDENSER CURRENT METHOD FOR THE DETERMINATION OF WAVE FORM AND MAXIMUM VALUE OF ALTERNATING CURRENT AND ELECTROMOTIVE FORCE.

Wave Form of Electromotive Force.—A condenser C is connected across the line, xy, the voltage of which is to be determined. The condenser current is commutated and is measured by a suitable milliammeter, millivoltmeter, or low-resistance galvanometer, G, as shown in Fig. 5. The sensitiveness of the arrangement can be varied by changing the value of the capacity, C, or by means of a resistance in shunt with the galvanometer on either the galvanometer side or line side of the commutator.

FIG. 5.



Condenser current method.

G is calibrated so as to give current in ampères. Let A be the current reading of the instrument thus calibrated, and let n be the frequency of the circuit.

If readings A are taken for successive positions of the commutator brushes, the instantaneous value of the line voltage corresponding to any reading is

$$e = \frac{A}{4nC}.$$

This determines the wave form of voltage.

For accuracy the resistance r of the galvanometer circuit, including the commutator, should be small compared with the reactance x of the condenser. There is little difficulty in selecting an instrument and a capacity so that this condition will hold. Where a number of current and voltage curves are to be taken and their phase positions are to be accurately determined, for greatest accuracy r/x should have the same value in taking each curve,—*i.e.*, when x is changed r should be changed to correspond, but in most cases this refinement is unnecessary. Thus, taking a case in which $r = 2.75$ ohms, $C = 0.4$ m.f., and $n = 60$,

we have $x = 6640$ and $r/x = 0.0004$. The phase shifting of the condenser current due to r is $\tan^{-1} r/x$, a little over one minute. The impedance ($\sqrt{r^2 + x^2} = 6640.00057$) is practically determined by x alone, the resistance having negligible effect on the impedance and on the amplitude of the current.

In range and in sensitiveness the condenser current method surpasses all other methods. The voltage may be a fraction of a volt or the highest voltage obtainable; with suitable shunts a current of practically any magnitude can be measured.

Wave Form of Current.—To determine the wave form of current, a resistance, or so-called shunt, R, is connected in series with the line. The condenser C is connected across its terminals, the commutated condenser current being measured by the galvanometer G. The wave form of current is thus determined in the same manner as the wave form of voltage.

Maximum Values.—The maximum value of current or voltage is determined by the maximum reading of the instrument,—that is, by the average value of the condenser current,—and, as already mentioned, a non-synchronous commutator may be used in this determination. The condenser current method may well be used for testing the maximum values of very high voltages, as in insulator testing.

Proof.—The relation at any instant between the charge q of the condenser and the current i is $dq = i\,dt$. During any time interval of half a period T,—that is, from any time $t = t_1$ to $t = t_1 + \frac{T}{2}$,—the charge changes from $+q$ to $-q$, the positive and negative waves being similar. Integrating for half a period, we have

$$\int_{+q}^{-q} dq = \int_{t_1}^{t_1 + \frac{T}{2}} i\,dt .$$

But the reading of the galvanometer or millivoltmeter, calibrated to read ampères in R as described above, is

$$A = \frac{2}{T} \int_{t_1}^{t_1 + \frac{T}{2}} i\,dt ,$$

this being the average value of the current during a half cycle subsequent to any time t_1. Hence we may write

$$2q = \frac{TA}{2}; \text{ or, } q = \frac{TA}{4}.$$

Writing $1/n$ for T, and Ce for q, we have

$$e = \frac{A}{4nC}.$$

The equation for e depends upon C being constant, which is true for an air condenser and practically true for a mica condenser. For a condenser with an inferior dielectric this relation is not true, and for such a condenser the method is correct for determining the instantaneous values of q but not of e. If the instantaneous values of e were accurately determined by some other method, data would be thus obtained for plotting a possible dielectric hysteresis loop * between q and e.

VII. CONDENSER DISCHARGE METHOD FOR THE DETERMINATION OF WAVE FORM AND MAXIMUM VALUE OF ANY PERIODICALLY VARYING ELECTROMOTIVE FORCE OR CURRENT.

Wave Form of Electromotive Force.—For determining the instantaneous values of any periodic electromotive force or current by the method of condenser discharge, the commutator is used not as a rectifier but as a synchronous switch for charging a condenser and discharging it through a galvanometer at a definite time in each cycle. A mica condenser should be used, or one in which the absorption is negligible. The arrangement of circuits is shown in Fig. 6. Bearing on the slip rings are the two brushes b b'; bearing on the commutator is the single brush B. (Any idle brush should be removed.) As the commutator is driven synchronously, it will be seen that the condenser is charged from the line until a definite instant in each cycle, depending upon the position of the brush B, and is then discharged through the galvanometer G. The reading of G depends upon the charge of the condenser, and hence upon the line voltage, at the last instant of charging. By setting B successively in dif-

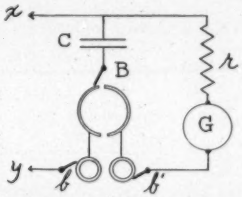
* Such a loop is given by Bedell, Ballantyne and Williamson, *Phys. Rev.*, vol. i, p. 81, 1893; *Trans. A. I. E. E.*, vol. x, p. 525, 1893; also Nichols' "Laboratory Manual," vol. ii, p. 193.

ferent positions and taking corresponding readings of G, the complete wave form can be determined.

The instrument G should be well damped. In determining wave form of voltage, a Weston voltmeter may be used, or a millivoltmeter with resistance r in series. To allow time for the condenser to discharge, it is desirable (although not necessary) to have the time-constant—resistance times capacity—of the discharge circuit less than one-half period. No resistance should be placed on the line side of the condenser or commutator. Calibration for voltage or current is made with direct current with the commutator running at proper speed.

The condenser discharge method will be found generally convenient through a moderate range on account of its easy calibra-

FIG. 6.



Synchronous switch and condenser discharge method.

tion and its applicability to any periodic current or voltage, there being no limitation to symmetrical alternating current waves. It cannot be used directly on a very high voltage circuit, as can the condenser current method. On such a circuit a high resistance should be bridged across the line, the apparatus shown in Fig. 6 being tapped off of part of it. On an alternating current line a transformer or auto-transformer can be thus used.

The alternate sets of commutator segments need not be of equal length in the condenser discharge method, as required in all the preceding methods; nor need the number of segments be identical with the number of poles. Thus, a commutator with two segments driven by a four-pole synchronous motor would charge the condenser for two half cycles and discharge it for two half cycles, if the segments were equal. This flexibility in equipment may at times prove a convenience.

Wave Form of Current.—For determining the wave form of

current a non-inductive resistance is placed in series with the circuit under test, the apparatus as shown in Fig. 6 being connected to the terminals of this resistance. In current measurements a galvanometer or millivoltmeter may be used; the resistance r should be small or omitted entirely.

Maximum Values.—Maximum values are determined by the maximum readings, as already discussed in Parts V and VI.

VIII. DETERMINATION OF PHASE DIFFERENCE.

The difference in phase between two alternating waves may be determined by ascertaining the difference in phase between their zero points. Using the same method of measurement on the two waves (as the air transformer method, condenser current method, or condenser discharge method) and so far as possible the identical circuits and apparatus,* a zero setting is found first for one wave, then for the other, and their difference determined. This does not necessitate calibration nor the determination of the complete wave forms unless these should be desired in those cases in which the two wave forms are very different. In such cases, however, phase difference has no exact significance, except by special definition. Instead of setting for zero, it is sometimes convenient to take a reading on each side of zero and to locate the zero by a plot or by interpolation.

Another method, sometimes adequate, is to make use of the methods of measurements described in Part I for the determination of average value of current or voltage. With the apparatus thus set up, zero settings are made first on one circuit and then on the other and the phase difference determined. The phase difference between two quantities thus determined means the phase difference between their median lines—lines dividing their wave areas in half. If the two waves have the same shape, the phase difference between their median lines will be the same as the phase difference between their zeros; if they do not have the same shape, the significance of phase difference is questionable, as already pointed out.

* When changes are made, they should be so made as to obtain relative accuracy in phase; thus, in the condenser current method, for example, any change in reactance should be accompanied by a compensating proportional change in resistance.

Other methods may be employed that are beyond the scope of the present paper. The methods here briefly described are incapable of any such accuracy as that attained, for example, in the several special methods for determining phase difference in instrument transformers now in use in some of our testing laboratories; but, while they are not precision methods, they are adequate for certain general purposes.

IX. GENERAL AND HISTORICAL.

The object of this paper has not been to give the results of investigations made by means of the synchronous commutator, nor to give a detailed description of a particular form of apparatus, but rather to give a statement of the various methods of its use. Several forms of apparatus will be found described in the references given below. The commutator, as described in this paper, makes use of the complete alternating current wave by reversing the circuit connections every half wave. A simpler form of apparatus *suppresses* alternate half waves instead of reversing them. Such an apparatus, which may well be termed a *suppressor,* will be found described in several of the references given. For a two-pole machine, a suppressor may consist of two brushes, side by side, resting upon a cylinder mounted upon the shaft of the machine. One-half the cylinder (180°) is conducting, the other half being non-conducting, so that the circuit between the two brushes will be closed during alternate half cycles. A suppressor may be placed in *series* or in *shunt* with a galvanometer, thus suppressing alternate half waves either by opening the galvanometer circuit or by short-circuiting it. With a suppressor the galvanometer becomes less sensitive than with a rectifying commutator; furthermore, a suppressor cannot be used for the condenser discharge method, nor can a series suppressor be used with the condenser current method. On the other hand, with a suppressor, calibration in some cases is simpler and short-circuiting, that may give trouble with a commutator, becomes impossible. The commutator described in this paper may be used as a suppressor by using two brushes, *b B,* only, the other brushes being removed.

The method for determining the wave form of flux and the air transformer method for determining the wave form of cur-

rent and voltage are mentioned by Sahulka [1] (who illustrates diagrammatically a non-synchronous suppressor that with a four-pole machine suppresses seven half waves and retains one) and are fully developed and described by Townsend,[2] who gives experimental results and a discussion of the theory of the methods. A synchronous commutator for the same purpose is described by Lyle [3] and by Lloyd and Fisher.[7] Townsend mentions the possibility of determining curves of quantity; this and the question of a hysteresis loop for a condenser is taken up in the discussion of his paper. Sumpner [5] has made use of a suppressor and galvanometer for measuring the average value of very small alternating currents, not otherwise measurable, and for determining form factor. Hospitalier [4] made use of a non-synchronous commutator with unequal segments for condenser discharge in operating his ondograph, and later Robinson [6] made similar use of a synchronous commutator, also with unequal segments, in operating the wave-meter of the General Electric Company. Robinson,[8] and Sharp and Crawford,[9] describe forms of synchronous commutators and the use of a direct current galvanometer as a zero instrument in alternating current testing. Sharp and Crawford employ not the usual revolving commutator but a reversing switch operated by a revolving cam. Chubb and Fortescue [11] have recently made use of a synchronous and also a non-synchronous suppressor in parallel with a galvanometer and in series with a condenser for measuring maximum voltages of very high value, but they make no mention of the determination of wave form. Measurements were made by them up to several hundred thousand volts by using an air condenser, one member of which was fifteen feet in length. The measuring apparatus was grounded and protected by shields, also grounded. Bedell [12] describes the condenser current method for determining wave form as here given. Morrison [10] describes a more elaborate form of commutator for integrating waves in which even harmonics are present.

The underlying principle developed in these methods is as follows:

To obtain the wave form of a quantity, this quantity is first differentiated with respect to time (by some inductive or other device) and is then integrated by a galvanometer, the desired limits of the integral being assigned by the commutator. The

procedure may be extended to other quantities than those described.

For determining wave form of current and voltage, the commutator methods here described—employing a contact of definite duration—are superior in reliability and in sensitiveness of instrument reading to the well-known methods of instantaneous contact employing a contact of infinitely short duration. Some quantities, as flux, readily determined by the commutator can at present be directly determined by no other method.

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BIOCHEMICAL STUDIES OF CHOLESTEROL.*

BY

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I. INTRODUCTION.

ORGANIC CHEMISTRY OF CHOLESTEROL.

CHOLESTEROL belongs to the class of lipins,† and is widely distributed throughout the animal world. Chevreul,[1] the Father of the Chemistry of the Fats, prepared pure cholesterol from human biliary calculi, and attempted to saponify it by prolonged heating with a solution of potash in a mixture of alcohol and water, but without success. From this experiment doubtless arose the term "unsaponifiable fat" which is occasionally applied to cholesterol and certain closely-related compounds.

Berthelot[2] recognized cholesterol as a monatomic alcohol, and prepared certain of its esters; he suggested that cholesterol

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† According to the classification of Rosenbloom and Gies (*Biochemical Bulletin*, 1911, i, 52), the *lipins* are divided into natural and artificial lipins.

The *natural lipins* include aliphatic and carbocyclic lipins, as well as lipins of undetermined constitution.

The *aliphatic lipins* are subdivided into simple and conjugate lipins. The *simple lipins* include the natural fats, fatty oils, waxes, fatty acids, soaps and higher monohydric aliphatic alcohols. The *conjugate lipins* include *proteolipins* such as ovovitellin, *glycolipins* such as cerebrogalactosides, *phospholipins* such as lecithin, and *glycophospholipins* such as carnaubon.

The *carbocyclic lipins* include the *sterols* (cholesterol, phytosterol, isocholesterol, coprosterol), the *esterols* or natural sterol esters, and the *cholates* (cholic, choleic, glycocholic, taurocholic acids).

The natural *lipins of undetermined constitution* include *chromolipins* such as lipochrome, and *miscellaneous lipins* "of uncertain qualities or doubtful existence."

The *artificial lipins* include synthetic esters, glycerides, soaps, metallic derivatives of the lipin alcohols (*e.g.*, sodium cholesterylate), compounds of lecithin (*e.g.*, with strychnine), and many other laboratory products.

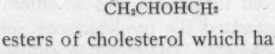
The sterols and the conjugate lipins are sometimes classified together as *lipoids*.

is related to both the aliphatic and aromatic series. Planer [3] prepared cholesteryl chloride from cholesterol by means of phosphorus pentachloride, while Diels and Abderhalden [4] obtained the same compound by use of thionyl chloride. Lindenmeyer [5] prepared sodium cholesterylate by the action of metallic sodium on a saturated solution of cholesterol in naphtha; while potassium cholesterylate was obtained by Obermüller [6] by the action of metallic potassium on a solution of cholesterol in ether. According to Walitzky,[7] cholesteryl chloride reacts with aniline, when their mixture is heated in a sealed tube, and gives rise to cholesteryl aniline; while it reacts with *p*-toluidine under these conditions to form cholesteryl toluidine.[7] A similar compound is obtained by the action of α naphthylamine or cholesteryl chloride. Bloch [8] heated anhydrous cholesterol with phenyl isocyanate: the product was cholesteryl phenylurethane. Mauthner and Suida [9] subjected a mixture of anhydrous cholesterol and anhydrous cupric sulphate to a temperature of 200°: a mixture of cholesteryl ether—dicholesteryl oxide—and cholesterilene—a hydrocarbon—was formed; the cholesterilene was removed by solution in benzol, and the ether was recovered from the residue by solution in a mixture of equal parts of benzol and absolute alcohol. These reactions demonstrate that cholesterol is an alcohol; the following reactions prove that it is a secondary alcohol. Diels and Abderhalden [4] oxidized cholesterol to a ketone of the same carbon content, cholestenone, by means of cupric oxide at a temperature of 280–300°. Windaus [10] subjected cholestenone to oxidation by neutral potassium permanganate and obtained a monocarboxylic ketonic acid, the molecule of which contained one atom of carbon less than did the molecule of cholesterol and that of cholestenone. Dorée and Gardner [11] have obtained this monocarboxylic ketonic acid from cholestenone by converting the latter into its ozonide and oxidizing the ozonide with dilute hydrogen peroxide and sulphuric acid.

Cholesterol contains at least one double bond. Wislicenus and Moldenhauer [12] found that, in solution in carbon disulphide, cholesterol adds bromine to form crystalline cholesterol dibromide; while Mauthner and Suida [13] state that cholesterol, in solution in chloroform, adds dry chlorine to form cholesterol dichloride. Lewkowitsch [14] converted cholesterol into choles-

terol-diiodide by means of Hübl's iodine reagent. Mauthner [15] prepared crystalline cholesterol hydrochloride (chlor-cholestanol) by passing hydrogen chloride gas into a solution of cholesterol in a mixture of absolute alcohol and ether. Willstätter and Mayer [16] passed a slow stream of hydrogen through an ethereal solution of cholesterol in the presence of platinum black sponge; each molecule of cholesterol added a molecule of hydrogen and thus gave rise to dihydrocholesterol, which does not add bromine. According to Dorée and Gardner,[11] cholesterol forms a monoözonide. These reactions show the presence of one ethylene bond in the cholesterol molecule; and the investigators, already mentioned, who have prepared the monocarboxylic ketonic acid from cholestenone, point out that the formation of this acid is evidence of the existence of this ethylene bond in a terminal vinyl group of a side chain of the cholesterol molecule. Other reactions indicate the possible existence of more than one double bond in cholesterol. Molinari and Fenaroli [17] found that cholesterol forms a diozonide, while Dorée and Gardner [11] obtained a diozonide of cholestenone. Willstätter and Mayer [16] oxidized dihydrocholesterol with chromic and glacial acetic acids and obtained a ketone, β-cholestanone, which adds bromine.

The molecular formula of cholesterol, according to Mauthner and Suida,[18] is $C_{27}H_{44}O$. Windaus [19] gives the molecular formula as $C_{27}H_{46}O$, and the structural formula as:



Of the many esters of cholesterol which have been prepared, the benzoate is of deep interest to the student of quantitative analysis, for Dorée and Gardner [20] have used it in the quantitative determination of cholesterol. Cholesteryl acetate is of value to the bromatologist, for on the melting-point of pure cholesteryl acetate and of pure phytosteryl acetate depends the method of Bömer [21] for the detection of the adulteration of animal fat by means of vegetable fat.

ZYMOCHEMISTRY OF CHOLESTEROL.

According to Schultz,[22] a ferment or enzyme, which produces hydrolysis of cholesteryl esters, exists in a mixture of

the whole blood and liver brei of horses and of cattle; the hydrolysis does not occur when either blood-plasma or blood-serum is substituted for whole blood. In connection with enzymes, it is of interest to note that Brücke [23] found that freshly-precipitated cholesterol adsorbs pepsin, a phenomenon which is still utilized in the study of that enzyme.[24]

Since Glikin [25] has reviewed the earlier work on cholesterol, it is necessary to discuss only the more recent work in this place.

SOLUTIONS OF CHOLESTEROL.

The solutions of cholesterol have recently been studied by several investigators. Porges and Neubauer [26] prepared a colloidal solution of cholesterol in water. Their technique was as follows: A solution of cholesterol in acetone was poured into water carefully and in small portions in order to avoid flocculation. As soon as a somewhat dense cloudiness appeared, the acetone was evaporated at a gentle heat on the water-bath, avoiding too rapid evaporation. This procedure was repeated until a colloidal solution of the desired concentration was obtained; any individual flakes were removed by filtration through thin paper, and a dense, milky, permanent suspension was obtained. The cholesterol behaved as a typical suspension colloid.

Porges and Neubauer [27] have also studied the behavior of alcoholic solutions of cholesterol with alcoholic solutions of metallic salts and of ethereal solutions of cholesterol with ethereal solutions of metallic salts. Since no precipitation occurred under these conditions they consider that cholesterol forms true solutions when dissolved in alcohol and in ether.

Loewe [28] investigated the properties of solutions of cholesterol in organic solvents. Dissolved in chloroform, cholesterol showed the normal behavior of a crystalloid by its influence on the surface tension of the solution; it also elevated the boiling-point of the solution and did not cause foaming. Cholesterol gave rise to a true solution when dissolved in petroleum ether, chloroform, or alcohol, as was shown by the vapor pressure of these solutions. The solutions of cholesterol showed the Tyndall phenomenon, and its solutions in chloroform, carbon tetrachloride, benzol, ether, and petroleum ether, especially when concentrated, contained ultramicroscopic particles, although not in such abundance as did the solutions of other lipoids like

lecithin. Loewe suggests that cholesterol is a semicolloid and should be classified as a semilipoid.

Gies [29] and Rosenbloom [30] have discovered that cholesterol and its esters with benzoic, oleic, palmitic, and stearic acids are able to diffuse from ether through a rubber membrane into ether.

CHOLESTEROL AND IMMUNITY.

Cholesterol also plays a rôle in immunity. Free cholesterol prevents the hæmolysis of red blood-corpuscles by saponin. According to the experiments of Windaus,[31] the cholesterol combines with the various saponins and thus exerts an antitoxic action, for the compound of saponin and cholesterol is without hæmolytic power. Thus one molecule of digitonin (a saponin) and one molecule of cholesterol unite to form a stable addition product. Esters of cholesterol are not antitoxic and do not form addition compounds with digitonin. In paroxysmal hæmoglobinuria an autohæmolysin is present in the blood-serum; and Pringsheim [32] has had recourse to intramuscular injections of cholesterol in combating attacks of this disease. Richter [33] has used cholesterol in the treatment of pernicious anæmia.

Robertson and Burnett [34] injected cholesterol into carcinoma of white rats during the premetastatic stage and obtained "a very notable acceleration of the primary growth." During the metastatic stage cholesterol failed to cause an increased growth of the primary tumor, but gave rise to a marked tendency to form metastases and to increase the rate of metastatic growth.

The function of cholesterol as an antigen, in the serum reaction of Wassermann for the detection of *Spirochæte pallida*, has been studied by Desmouliére.[35] The liver of a syphilitic or of a normal human being—adult or child—or of a pig is ground and rendered lipin-free by extraction with successive portions of ether. The residual tissue is dried in the air, then at 37° C., and is extracted by maceration with absolute alcohol at the latter temperature. The alcoholic extract is removed by filtration and lacks antigenic power; it dissolves cholesterol, which is not precipitated by dilution with physiological salt solution; and the resulting liquid possesses antigenic power to a high degree, giving positive reactions even with the sera of former syphilitics, where the customary Wassermann reaction usually gives a negative result. With sera of non-syphilitics the reac-

tion is always negative. Dextrogyrate isocholesterol also produces complement deviation, when substituted for cholesterol; however, the reaction is far less sensitive than that produced by lævogyrate cholesterol.

CHOLESTEROL IN THE BLOOD.

During disease the cholesterol content of the blood may change. Grimbert and Laudat[36] state that the total cholesterol of the serum increases during Bright's disease, nephritis, and syphilitic nephritis. It also increases after ingestion of fat in both healthy people and nephritic patients. Weston and Kent[37] report that the total cholesterol of the serum of lunatics does not differ from that of the serum of normal subjects. From the researches of Hermann and Neumann[38] it follows that the whole blood of normal women, of pregnant women, and of newly-born children contains the same quantity of free cholesterol, expressed in grammes per litre. However, the quantity of cholesteryl esters is much higher in pregnant women's whole blood, and much lower in the whole blood of new-born children, than it is in the whole blood of normal women.

CHOLESTEROL IN THE LOWER ANIMALS.

The occurrence of cholesterol throughout the entire animal world has been studied by Dorée,[39] who found cholesterol in the following animals: rabbit, grass snake, mackerel, whelk, crab, cockroach, earth-worm, and sea anemone. Cholesterol-like substances were found in the silkworm moth, starfish, and sponges.

PHYTOSTEROL IN METABOLISM.

That the phytosterol of the food can not pass over into the animal fat has been demonstrated by the researches of Virchow[40] on dogs and swine, and of König and Schluckebier[41] on swine. The latter investigators suggest that the phytosterol may be changed into cholesterol within the body, possibly in the intestine. They found that, during certain diets of vegetable origin, a reduction of phytosterol to coprosterol may take place in the digestive tract, and either or both these alcohols may occur in the fæces. Fraser and Gardner[42] have shown that the phytosterol of the food does not appear in the blood stream,

but that a ration containing phytosterol and no cholesterol does give rise to an increase in the quantity of free cholesterol of the blood.

FATE OF CHOLESTEROL IN THE ANIMAL BODY—THE STEROLS OF THE FÆCES.

Many researches have dealt with the absorption and fate of cholesterol in the animal body; certain of these investigations will now be reviewed. In the human digestive tract cholesterol may be reduced to coprosterol, which is a dihydrocholesterol—metameric with the dihydrocholesterol of Willstätter and Mayer.[16] Coprosterol was first isolated from human fæces by Flint,[43] who named it stercorin. It was termed coprosterol by von Bondzynski and Humnicki,[44] who ascribe its formation to putrefactive processes in the intestine. They found that a healthy man excreted ingested cholesterol in large part as coprosterol in the fæces. A further study of coprosterol has been made by von Bondzynski.[45] Flint [46] states that only cholesterol is found in the fæces of fasting animals and in the meconium; stercorin is absent. The researches of Müller [47] confirm the view that cholesterol is reduced to coprosterol by intestinal putrefaction. Since an absolute milk diet is one of the best means of limiting putrefaction of protein in the intestine, the excretion of unchanged cholesterol in the fæces of subjects kept on such a diet would demonstrate that the normal reduction of cholesterol to coprosterol is due to intestinal putrefaction. Cholesterol occurred in the fæces of a breast-fed infant, of two bottle-fed infants, of a sucking calf and of two adults on a milk diet, as well as in meconium. Coprosterol occurred in the fæces of an adult on a meat diet and of an adult on a mixed diet. These results strengthen the theory of reduction by intestinal putrefaction. The occurrence of cholesterol in meconium is ascribed to lack of bacterial decomposition in the fœtal intestinal canal.

In the fæces of the horse von Bondzynski and Humnicki [44] discovered hippocoprosterol, which they considered to be a reduction product of cholesterol. Dorée and Gardner [48] have demonstrated that hippocoprosterol is not a product of animal metabolism, but is an alcohol, $C_{27}H_{56}O$ or $C_{27}H_{54}O$, which occurs in grass and passes through the digestive tract unchanged.

They propose for it the name chortosterol. These investigators never found cholesterol in the fæces of herbivora.

In the fæces of the dog von Bondzynski and Humnicki [44] found cholesterol; while Kusumoto [49] states that both cholesterol and coprosterol are present in dog fæces. According to Kusumoto,[50] during a meat diet less cholesterol was excreted in the fæces than was contained in the food; the same result was obtained when cholesterol was added to the ration. The lost cholesterol may be absorbed or may be destroyed by putrefaction. The experiments of Dorée and Gardner [20] show that the dog usually excretes cholesterol of the food as such in the fæces; however, during a diet of raw brains of sheep the cholesterol is excreted as coprosterol.

Ellis and Gardner [51] have studied the excretion of cholesterol in the fæces of the cat. On a meat diet the cholesterol is reduced to coprosterol, but the reduction is not always complete, for a mixture of the two alcohols may be excreted; a portion of the cholesterol disappears in the digestive canal. When cholesterol was added to a ration composed of mixtures of white bread, egg white, wheat germ extracted with ether, and purified suet, cholesterol was excreted unchanged. When phytosterol was added to the ration, unchanged phytosterol was found in the fæces.

THE ABSORPTION OF CHOLESTEROL.

Jankau [52] introduced cholesterol into the stomach of rabbits; only a portion of it appeared in the fæces. The remainder must have been absorbed, yet did not appear in the bile and could not be found in the blood several hours after feeding. Injected subcutaneously into rabbits, cholesterol was absorbed, but soon vanished from the blood stream without appearing in the bile. In the case of dogs, cholesterol mixed with the food was well absorbed by the intestine, but did not increase the cholesterol content of the bile. Subcutaneous injection of cholesterol into dogs also failed to increase the cholesterol content of their bile. According to Goodman,[53] intravenous injection of cholesterol into a dog did not increase the total volume of the fistula bile or the total quantity of cholesterol and of cholic acid in the bile. The same investigator found that a diet rich in protein increased the total output of bile, and the total quantity and

concentration of both the cholesterol and cholic acid. A diet of brain, with its high cholesterol content, did not produce any greater excretion of cholic acid in the bile than did a diet of egg albumin, which contains merely a trace of cholesterol. Pribram[54] introduced cholesterol and its esters into the stomach of rabbits and was able to demonstrate that cholesterol was absorbed and occurred in increased quantity in the blood. Moreover, the serum of a rabbit which had been fed cholesterol was able to prevent hæmolysis of red corpuscles by saponin, while the serum of a normal rabbit permitted such hæmolysis; hence, at least the greater portion of the absorbed cholesterol was in the serum and in the free state, since cholesteryl esters do not prevent hæmolysis.

Dorée and Gardner [55] have evolved a theory concerning the cholesterol of the animal body. Cholesterol is a constant constituent of all cells and is not excreted as a waste product on the breaking down of a cell by life process, but is used again in the formation of new cells. The liver breaks down dead cells—for instance, blood-corpuscles—and eliminates their cholesterol in the bile. In the intestine the cholesterol is absorbed, probably as esters, along with the bile-salts, and is carried by the blood for incorporation in new cells. This is opposed to the view of Stadelmann,[56] who maintained that a circuit of the cholesterol with the bile in no case exists.

From experiments, Dorée and Gardner [55] concluded that rabbits excrete cholesterol only when it is fed to them, and that they absorb about one-half of the ingested cholesterol. The dog and the cat also absorb cholesterol from their food. The quantity of cholesterol in the blood of a rabbit was increased by addition of cholesterol to the diet. Fraser and Gardner [57] found that the power of saponin to produce hæmolysis of rabbit erythrocytes was counteracted by the sera of rabbits which had been fed cholesterol, cholesteryl oleate or stearate, or phytosterol; the sera retained their antihæmolytic power after exposure to a temperature of 56° C. for one hour. The serum of a normal rabbit was always used for a control. The experiments demonstrate that ingested cholesterol is absorbed in part and occurs in the blood in the free state; while ingested cholesteryl esters undergo hydrolysis during the process of digestion, and their cholesterol appears, at least in part, in the blood stream in the

free state. The amount of cholesterol which found its way into the blood stream was not increased by increasing the quantity of it in the ration; hence, the rabbits probably absorbed only so much cholesterol as they could utilize. A further study by Fraser and Gardner [42] has revealed the rôle of phytosterol in increasing the antihæmolytic power of the serum. When rabbits are fed a cholesterol-free diet containing phytosterol (ordinary bran), phytosterol does not appear in the blood as such, but the quantity of free cholesterol in the blood increases. Both the free cholesterol and the cholesteryl esters are greater in quantity in the blood of rabbits fed ether-extracted bran plus cholesterol than in the blood of rabbits fed only the extracted bran. The ingested cholesterol gives rise to an increase in both the free and esterified cholesterol of the blood.

Ellis and Gardner have studied the influence of various diets and of inanition on the cholesterol content of the liver [58] and of other organs [59] of rabbits. A diet of green food containing phytosterol gave rise to a slight increase in the cholesterol content of the liver. The total quantity of cholesterol in the liver underwent a marked increase on a diet of ether-extracted bran plus cholesterol, and also after intraperitoneal injection of cholesterol. During inanition the rabbits lived on their own tissues and stored cholesterol in their livers, while the content of their blood in both free and total cholesterol underwent an increase. The cholesterol content of the blood of rabbits depended on the sterol content of their food. In the case of muscle, kidney, and lung, the quantity of cholesterol was apparently independent of the sterol content of the diet. Starvation caused an increase in both total and esterified cholesterol of the kidney; while intraperitoneal injection of cholesterol gave rise to an abnormally high content in cholesteryl esters in that organ. Inanition, as well as intraperitoneal injection of either olive oil or olive oil plus cholesterol, led to an increase in the total cholesterol content of the bile.

CHOLESTEROL IN INCUBATION AND AUTOLYSIS.

Ellis and Gardner [60] determined the total quantity of cholesterol in eight individual eggs, eight individual chicks, a set of six eggs and a set of six chicks. The chicks were freshly hatched. The analyses failed to reveal any gain in cholesterol

during incubation. "In the differentiation of the ovum into the complex aggregates of cells constituting the chick no formation of cholesterol takes place."

Corper [61] has studied the influence of autolysis upon cholesterol. During the autolysis of dog spleen the cholesterol in that organ is not changed.

CHOLESTEROL IN PATHOLOGY.

Windaus [62] has demonstrated that the free cholesterol content of normal and pathological (amyloid or fatty-degenerated) human kidneys is about the same, but that the diseased kidney contains far more cholesteryl esters (oleate and palmitate) than are present in the normal kidney.

Duranton [63] has made an extensive study of the action of microörganisms on ox bile with special reference to the deposition of cholesterol. After filtration and sterilization, portions of the bile were sown with pure cultures of the organisms in bouillon and incubated at 37° C. Sterile control experiments were also carried out. *B. coli, B. typhosus* of Eberth, two strains of *B. paratyphosus, B. diphtheriæ* of Löffler, *B. pyocyaneus, B. subtilis,* and *Staphylococci* produced precipitates in which cholesterol crystals were present. *B. pyocyaneus* caused the deposition of crystals as early as the fifteenth day; while in the case of *Staphylococci* the crystals appeared on the sixtieth day. Under anaërobic conditions, *B. tetani, B. putrificus, B. coli,* and *B. pyocyaneus* gave rise to a deposit of cholesterol crystals. *B. coli* and *B. pyocyaneus* precipitated the cholesterol more rapidly under anaërobic conditions than in an aërobic environment. The appearance of cholesterol crystals was always preceded by the formation, in the culture-tubes, of a precipitate which responded to Pettenkoffer's reaction and, therefore, consisted of bile-acids. However, *B. paratyphosus* and *B. coli* did not modify the alkalinity of the bile; *B. typhosus* and *B. diphtheriæ* diminished the alkalinity to but a very slight extent; and *B. pyocyaneus* increased the alkalinity in a high degree. *B. typhosus, B. coli* and *B. pyocyaneus* were grown on bile for two days; the cultures sterilized in the autoclave at 100° C. for fifteen minutes and then returned to the incubator. No precipitates were formed, proving that the microörganisms do not act mechanically as foreign bodies, causing a precipitation of choles-

terol from the bile. The toxins of *B. diphtheriæ, B. tetani, B. typhosus,* and *B. coli* were permitted to act on bile; the precipitate formed more rapidly than when bouillon cultures of the organisms themselves were used, and cholesterol crystals were always present, although not so plentifully as in the experiments with the living organisms.

Duranton concludes that under the influence of microorganisms decomposition of the bile-salts occurs, accompanied by a diminution of the quantity of bile-acids. Since the bile no longer contains sufficient bile-salts to hold the cholesterol in solution, the latter is precipitated. Most microörganisms possess this power, and apparently act by means of their toxins to decrease the content of the bile in bile-salts. In the formation of biliary calculi *in vivo* the leading rôle is played by microorganisms which have gained entrance to the bile and give rise to a precipitation of its cholesterol. The epithelial cells present play an entirely secondary rôle in the formation of calculi by acting as centres for the deposition of the cholesterol as it is precipitated.

Crystals of cholesterol have been found in the urinary sediment in cases of cystitis, pyelitis, chyluria, and nephritis.[104]

The influence of the subcutaneous injection of toluylene diamine (1 methyl 2, 4 diamino benzene) upon the excretion of cholesterol in the bile [64] and fæces [65] of dogs has been studied by Kusumoto. The quantity of cholesterol was increased, due to the increased destruction of red blood-corpuscles in the liver under the influence of the diamine.

NATURAL OCCURRENCE OF OXIDATION PRODUCTS OF CHOLESTEROL.

Lifschütz [66] has prepared oxidation products of cholesterol by permitting a solution of potassium permanganate in concentrated acetic acid to act upon a solution of cholesterol in glacial acetic acid at the temperature of the water-bath. Among the products of the reaction are oxycholesterol ether and oxycholesterol. If the formula of cholesterol be written $C_{26}H_{44}O$, then oxycholesterol ether is $(C_{26}H_{43}O)_2O$ and oxycholesterol is $C_{26}H_{44}O_2$. Each of these compounds dissolves in glacial acetic acid and then reacts with concentrated sulphuric acid to give a solution with a characteristic absorption spectrum. In the case

of oxycholesterol ether the absorption spectrum is characterized by a broad, deep-black band covering the entire yellow and part of the green and by a fine line in the red; while in the case of oxycholesterol it is characterized by a band in the red. Lifschütz [67] has also obtained these oxidation products of cholesterol by the action of benzoyl peroxide on the solution of cholesterol in glacial acetic acid, and has demonstrated their presence in wool fat,[66] in brain and in pancreas fat,[67] in bone fat and in the fat of fresh whole blood of cattle,[68] and in the fresh defibrinated blood of cattle.[69]

CHOLESTEROL AND THE BILE-ACIDS.

The relation of cholesterol to the bile-acids, cholic, choleic, taurocholic, and glycocholic acids, was first suggested by Berthelot,[2] and has recently been discussed by Goodman [53] and by Rosenbloom and Gies.[70]

II. THE PREPARATION OF CHOLESTEROL.

DESICCATION OF THE TISSUE.

Tissues, such as brain, must be dried before cholesterol can be extracted from them. Various procedures have been devised to prepare the tissues for extraction. Baumstark [71] removed the water from brains of horses, calves, sheep, and cattle by permitting the brains to remain in contact with ether, which was changed at intervals. The water was removed by diffusion, but the process required several months. The brains were then cut in slices one centimetre thick, and were extracted in the cold with ether for a period of two months. Bünz [72] mixed finely-divided horse brains with one and one-half times their quantity of anhydrous sodium sulphate and ground the resulting mass to a fine powder, which was extracted in the cold with ether. Rosenheim [73] mixed minced sheep brain with sand and three times its weight of plaster of Paris, permitted the mass to set, crushed it to a coarse powder, and extracted in the cold with acetone. Tebb [74] applied the method of Rosenheim to human brains. Fränkel and Elfer [75] mixed the tissue brei in a mortar with one-half its weight of anhydrous disodium monohydrogen orthophosphate at a temperature of about 40° C., transferred the mixture to a warm cloth, which was then placed in a warm

press in order to remove the liquid hydrated sodium phosphate—$Na_2HPO_4.12H_2O$—which had been formed at the expense of the tissue water and which melts at 35° C. The solid residue was permitted to cool, powdered, and extracted with petroleum ether. Rosenbloom [76] has quite recently recommended the use of calcium carbide as a dehydrating agent in the preparation of cholesterol from brain.

REMOVAL OF PHOSPHATIDES.

Zuelzer,[77] who worked on ox brain, devised a method for the separation of cholesterol from lecithin and other phosphatides. When an ether extract of brain, not too dilute, was treated with acetone until a precipitate no longer formed, the phosphorized compounds had been precipitated, while the cholesterol remained in solution in the mixture of ether and acetone.

SAPONIFICATION OF GLYCERIDES.

Baumstark [71] stated that the greater portion of the cholesterol is present in the brain in the combined state; the later work of Bünz [72] and of Tebb [74] has shown that the cholesterol of that organ is present entirely in the free state; and, in harmony with this, Ellis and Gardner [59] have proved that only free cholesterol and no cholesteryl esters exist in the brain of the rabbit. However, during the extraction of cholesterol, fats are also extracted and accompany the cholesterol even after the precipitation of the lecithin. These fats are best removed by saponification, and two reagents are available for this purpose—alcoholic potash and true sodium ethylate. Chevreul used boiling alcoholic potash for the saponification of glycerides, and the use of this reagent in fat chemistry has been emphasized by Koettstorfer.[78]

The use of sodium ethylate was introduced by Kossel and Obermüller;[79] in this mode of saponification the entire reaction is completed *in the cold*, at the temperature of the room, and therefore the new method has a marked advantage over the use of boiling alcoholic potash. Kossel and Obermüller state that, on addition of an alcoholic solution of sodium ethylate to the solution of a fat in ether, in a very short period of time—from several seconds to several minutes—a compact precipitate of the sodium soaps of the fatty acids is formed. If sufficient

sodium ethylate has been used, the saponification is completed in a short time at ordinary temperature and the soap separates in the form of a precipitate which may be removed without difficulty by filtration. The filtrate contains the cholesterol. The mixture should be permitted to stand for twenty-four hours before filtration. If either the quantity of sodium ethylate or the period of reaction be insufficient, new precipitates of soap are formed after filtration. It was ascertained by experiment that from 100 to 150 grammes of fat require for saponification approximately so much sodium ethylate as is formed by solution of 10 grammes of metallic sodium in 150 to 200 c.c. of absolute alcohol. It is recommended to use two-fold or three-fold this quantity of ethylate in a saponification.

Kossel and Krüger [80] have modified this procedure. They dissolve the fat in absolute alcohol and heat with the alcoholic solution of sodium ethylate on the water-bath, in order to hasten the saponification. The quantity of ethylate required for actual complete saponification of any given weight of fat is the quantity theoretically required by that weight of fat. If the reaction be carried out under a reflux condenser instead of in a vessel exposed to the atmosphere, either the period of the reaction must be lengthened or the quantity of ethylate must be increased in order to insure complete saponification of the fat. Kossel and Krüger always use a freshly-prepared solution of sodium ethylate, obtained by dissolving metallic sodium in absolute alcohol; each 100 c.c. of the solution contains 5 grammes of sodium; 5 grammes of fat require from 10 to 15 c.c. of this solution for their saponification.

Obermüller [81] has studied the mechanism of the reaction which occurs when sodium ethylate saponifies a glyceride. When the fat is dissolved in ether or in alcohol and is treated with an alcoholic solution of sodium ethylate, sufficient water must be present in order to produce saponification of the fat; otherwise the reaction does not occur at all or is incomplete. This water may be present in the alcohol (absolute alcohol contains but 99.4 to 99.8 per cent. of alcohol) or may be absorbed from the atmosphere. The fatty acid glyceride enters into a double decomposition with the sodium ethylate to form the ethyl ester of the fatty acid and the sodium salt of glycerol. The water decomposes the sodium salt of glycerol, and the products of the reac-

tion are glycerol and sodium hydroxide. The sodium hydroxide and the ethyl ester of the fatty acid now react to form ethyl alcohol and the sodium salt (soap) of the fatty acid. The reaction is most rapid with sodium ethylate, less rapid with sodium amylate, and still less rapid with sodium methylate—which may also be used for the saponification of fats.

CHOLESTEROL FROM BRAIN.

At some stage of the preparation of cholesterol heat has always been used—either during the extraction, or for the evaporation of the solvent, or during saponification for the removal of fatty matter. In the course of this research cholesterol has been prepared from brain in two ways: (*a*) During extraction and purification the temperature has never exceeded that of the body; (*b*) during the course of extraction and purification the temperature has exceeded that of the body only during the process of saponification by means of boiling alcoholic potash.

Preliminary Experiment.

Twenty-four brains from freshly-killed sheep, and retaining the animal heat, were cut into slices five millimetres in thickness by means of a sharp knife; the sliced brains were spread out in porcelain dishes and covered with alcohol; they were moved about and turned over from time to time in order to expose fresh surfaces to the dehydrating action of the alcohol. The alcohol was twice decanted, and replaced by a new portion, during the course of thirty-six hours. The brains were then dried between filter-paper and ground fine in a meat-chopper. The minced material was placed in a glass-stoppered bottle of ample size, covered with an excess of ether, and allowed to extract at the temperature of the room for a period of twenty-four hours, shaking at intervals. The ether was removed by decantation through a folded filter, and the insoluble material was permitted to drain on the filter. The residue was again extracted with ether for a period of twenty-four hours, and the insoluble residue from this extraction was subjected to a third extraction for the same period of time. Thus three ether extracts were obtained. Each of these was heated on the water-bath in order to remove the solvent, but the temperature had risen far above 37° C. long before all the solvent had vanished;

in fact, the full temperature of 100° C. was required to obtain a dry residue. The brains had retained alcohol and given it up to the ether.

Heating was therefore abandoned in the subsequent experiments. In order, however, to test the methods of purification—which will be described in detail in the section on "Preparation of Pure Cholesterol from Brain," and which will be outlined in Table III—the residues of the first and third extracts were studied separately. Each was dissolved in ether, the lecithin and its related compounds were precipitated by acetone and removed by filtration, and the filtrate was evaporated before an electric fan. The residue was divided into two equal portions, from one of which the fat was removed by saponification with alcoholic potash; from the other by saponification with sodium ethylate. The cholesterol thus obtained was further purified by recrystallization at room temperature from ether to which a small amount of alcohol had been added.

In the case of the first extract, the fraction saponified by alcoholic potash, as well as the fraction saponified by sodium ethylate, gave a deposit of crystals on both the bottom and the sides of the crystallizing dish. Far more lipochrome was present in the crystals on the side than in those on the bottom of the dish. The deposit of crystals on the side was removed by means of a scalpel, and it and the deposit on the bottom were recrystallized separately at room temperature from ether containing alcohol until pearly-white crystals—free from lipochrome—were obtained.

In the case of third extract, mechanical separation of the first crop of crystals into two fractions was not necessary. After saponification with alcoholic potash, the entire product was pure on the second crystallization. After saponification with sodium ethylate, pearly plates were deposited on the bottom of the dish on the fourth crystallization, while the lipochrome was concentrated in a slight crust of crystals on the side of the dish; this crust was discarded.

Of course, the mother liquors of the various crystallizations contained the major portion of the lipochrome, as well as of any aldehyde resins, formed by the action of the alkali on the alcohol during the process of saponification. The crystals were freed from mother liquor by washing with alcohol, and were

dried on filter-paper. The melting-point of each final product was determined with ordinary thermometers and corrected according to the formula of Bömer.[21] In Table I the corrected melting-points are given.

TABLE I.

MELTING-POINT OF CHOLESTEROL.

Preliminary Experiment.

Extract	Mode of saponification	Number of crystallizations	Corrected melting point, °C.
FIRST	Alcoholic potash	Bottom deposit crystallized twice.	147.6
		Side deposit crystallized thrice.	147.5
	Sodium ethylate	Bottom deposit crystallized twice.	147.0
		Side deposit crystallized twice.	147.6
THIRD	Alcoholic potash	2	147.7
	Sodium ethylate	4	147.3

Preparation of Pure Cholesterol from Brain.

The reagents used in these experiments will first be described. Alcohol was freshly-redistilled 95 per cent. alcohol. Alcoholic potash was a 4 per cent. solution of C. P. potassium hydroxide in alcohol; the hydroxide was ground to a fine powder in a mortar, then mixed with the alcohol; after several days the slight quantity of insoluble matter was removed by filtration through a folded filter. The filtrate was unusually pure; for a period of over three months it remained water-white without the faintest trace of yellow. Sodium ethylate was prepared as required by dissolving bright metallic sodium in absolute alcohol—ten grammes of metal to each 150 c.c. of solvent. Ether was absolute ether, redistilled over sodium. Acetone was redistilled as required, and the fraction boiling at 56 to 57° C. was collected for use. Hardened, smooth filter-papers were always used for filtrations.

Sheep brains, in sets of twenty-four, still retaining the animan heat, were cut, dehydrated with alcohol, and extracted with ether at the temperature of the room, as described in the preliminary experiment. Each set of brains gave rise to a series of three extracts. Four sets of brains were worked up; there-

fore twelve extracts were obtained. Each extract was placed in a flat-bottomed porcelain dish, which was slightly inclined toward an electric fan, so that the current of air generated by the fan would play over the surface of the liquid. As soon as a crust formed over the surface of the solution it was broken up with a glass rod. As evaporation advanced, the angle of inclination of the dish was increased; and when the solvent had entirely evaporated, the dish was placed at an angle of almost ninety degrees to the table in order to dry the residue, which was stirred with a glass rod to assist in the process. The residues consisted of yellowish semisolid masses. Each residue was transferred to a glass-stoppered bottle by means of a horn spatula. The four residues of the first extracts were finally combined, as were the four residues of the second extracts and the four residues of the third extracts. Thus three masses of lipins were obtained, each of which was derived from ninety-six sheep brains. Each mass was triturated in a mortar with successive portions of ether until it had been completely dissolved; as little ether as possible was used so that the solution would be practically saturated with lipins. The ethereal solution was transferred to a tall glass cylinder, and three-fold its volume of acetone was added slowly with constant stirring in order to precipitate the lecithin and its related substances. The mixture was permitted to stand over night. In the case of the first extract, the supernatant liquid was perfectly clear; in the case of the second extract and of the third extract, the supernatant liquid held in suspension minute particles; but in all three cases, after filtration through a folded filter, the filtrate was perfectly clear. The first extract yielded the most deeply colored filtrate, the third extract the least colored filtrate, while the color of the filtrate of the second extract lay between that of the other two.

Each filtrate was evaporated to complete dryness before an electric fan, the residues of crude cholesterol forming solid masses. The ninety-six brains had weighed 8294 grammes; the total weight of each of the three ether extracts, the weight of each residue of crude cholesterol, and its saponification number are given in Table II. Of each residue, one gramme was used for the determination of the saponification number; the remainder was divided into two equal portions, both of which were used for the preparation of pure cholesterol—one after saponi-

fication by means of sodium ethylate; the other after saponification by means of alcoholic potash. The saponification number (number of milligrammes of potassium hydroxide required for the saponification of one gramme of the crude cholesterol) was determined in the usual way by the method of the Association of Official Agricultural Chemists,[82] but, on account of the small weight of the sample, 0.4 per cent. alcoholic potash and 0.2 normal mineral acid were substituted for 4 per cent. alcoholic potash and 0.5 normal acid. The saponification numbers show that considerable saponifiable matter was present in all the residues; and, as was to be expected, the residue derived from the first extract had a higher saponification number and therefore contained more saponifiable matter than the residues derived from either of the other extracts. Each of the two modes of saponification for the preparation of pure cholesterol will now be described.

TABLE II.

ETHER EXTRACT OF SHEEP BRAIN.

8294 Grammes of Brain.

Extract	Ether extract		Crude cholesterol		Saponification number of crude cholesterol
	Weight in grammes	Per cent. of fresh tissue	Weight in grammes	Per cent. of fresh tissue	
FIRST	260	3.13	40.0	0.48	36.2
SECOND	173	2.09	27.5	0.33	25.6
THIRD	104.5	1.26	18.0	0.22	27.7

Saponification by Means of Alcoholic Potash.

The crude cholesterol was placed in an Erlenmeyer flask, and for each gramme of material 10 c.c. of alcoholic potash were added. The flask was heated on a water-bath beneath a reflux air condenser, and the solution was boiled for one hour after all the crude cholesterol had dissolved. As the contents of the flask cooled to the temperature of the room, a voluminous precipitate of crystalline cholesterol separated. The crystals were removed by filtration, the filtrate was transferred to a separatory funnel, diluted with three or four times its volume of water, and shaken with an ample volume of ether. After the mixture had separated into two layers, the aqueous layer was drawn off and again extracted with ether. The two ethereal

extracts were combined, and in them was dissolved the precipitate of cholesterol. The ethereal solution was washed with water in a separatory funnel, then evaporated before an electric fan. After the ether had disappeared completely, considerable alcohol was left in the porcelain dish. The cholesterol and this alcohol were transferred to an Erlenmeyer flask *and the process of saponification was repeated.* In order to avoid contamination of the ether with much alcohol, after filtering out the cholesterol crystals, the alcoholic filtrate was concentrated in a casserole on the water-bath to a volume of 25 c.c., diluted with 125 c.c. of water, and extracted with two successive portions of ether in a separatory funnel. The combined ether layers were used for dissolving the crystalline cholesterol, and the resulting ethereal solution was washed free from soaps by successive portions of water in a separatory funnel. A solution of calcium nitrate was used in testing portions of the wash waters for the presence of soaps. The wash waters were combined and extracted with ether, which was then washed free from soaps by means of water; this ether was then added to the main ether solution. The ether was permitted to evaporate spontaneously in the room. The residue was dissolved in as small a volume of ether as possible; the solution was filtered into a small crystallizing dish; the filter was washed with ether; a few cubic centimetres of absolute alcohol were added to the contents of the dish, which was covered with a watch-glass; and the solvent was allowed to evaporate slowly and spontaneously at room temperature. When the mother liquor amounted to about one-eighth of the volume of the original solution it was poured on a filter-paper on a Buchner funnel, the crystals were transferred to the filter, sucked free from mother liquor, and washed with alcohol. The crystals thus obtained were again subjected to the process of crystallization, and the entire procedure was repeated until a crop of crystals was obtained entirely free from lipochrome. These crystals were filtered and washed as described above, then placed on a pad of smooth filter-paper, beneath a bell jar, and permitted to dry in the air at the temperature of the room.

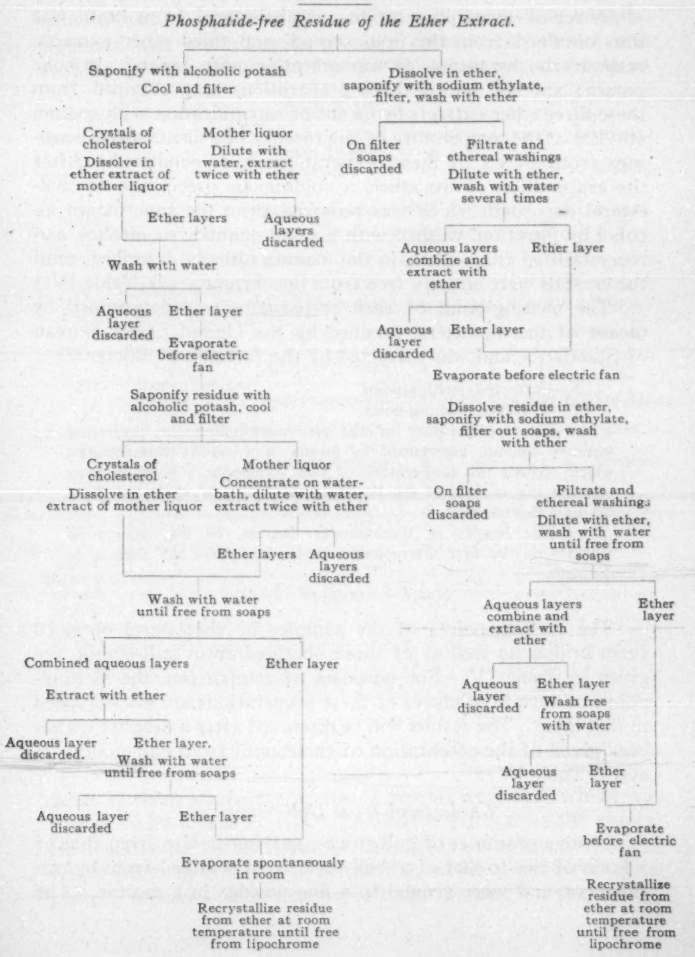
Saponification by Means of Sodium Ethylate.

The crude cholesterol was dissolved in ether in Erlenmeyer flasks of 500 c.c. capacity; in every case sufficient ether was

taken to insure at least three volumes of ether to one volume of ethylate solution in the final mixture. For each gramme of crude cholesterol, 3 c.c. of ethylate solution were used. This reagent was slowly added to the ethereal solution, the flask being given a rotary motion during the mixing. The contents of the flask were shaken at frequent intervals in the course of the first hour, and it was then permitted to stand for twenty-four hours. Even in the first few minutes after adding the reagent the saponification became apparent by the precipitation of soaps. The supernatant liquid was decanted through a filter on a Buchner funnel; the precipitated soap was also transferred to the filter and sucked free from solvent. It was then finely divided, shaken up with ether, and the washings thus obtained were filtered through a paper on the Buchner funnel and added to the filtrate from the soaps. The combined filtrate and washings were diluted with ether, and were washed with water several times in a separatory funnel in order to remove alcohol and soaps. The wash waters were combined and shaken with ether to recover any cholesterol; the ether was added to the main ethereal solution, which was now evaporated to dryness before an electric fan. *The residue was dissolved in ether and treated with sodium ethylate as before.* The small quantity of precipitated soaps was removed by filtration with the aid of a Buchner funnel, and the precipitate was washed on the filter with ether. The combined filtrate and washings were diluted with ether and were shaken with successive portions of water in a separatory funnel, until a portion of the wash water failed to yield a precipitate on the addition of a solution of calcium nitrate—thus showing that soaps had been completely removed from the ethereal solution. The combined wash waters were extracted in a separatory funnel with ether in order to recover cholesterol; the ether was washed with water until free from soaps, and was combined with the main ethereal solution, which was then evaporated to dryness before an electric fan. The residue was reddish-yellow in color and yielded a reddish-yellow ethereal solution; the color was much deeper than that of the residue obtained after saponification with alcoholic potash. This residue was recrystallized from ether at the temperature of the room, in the same manner as has already been described in detail in the latter portion of the preceding paragraph (*"Saponification by Means of*

TABLE III.

PREPARATION OF PURE CHOLESTEROL FROM PHOSPHATIDE-FREE ETHER EXTRACT OF BRAIN.


Phosphatide-free Residue of the Ether Extract.
Saponify with alcoholic potash
Cool and filter
Crystals of cholesterol
Dissolve in ether extract of mother liquor
Mother liquor
Dilute with water, extract twice with ether
Ether layers
Aqueous layers discarded
Wash with water
Aqueous layer discarded
Ether layer
Evaporate before electric fan
Saponify residue with alcoholic potash, cool and filter
Crystals of cholesterol
Dissolve in ether extract of mother liquor
Mother liquor
Concentrate on water-bath, dilute with water, extract twice with ether
Ether layers
Aqueous layers discarded
Wash with water until free from soaps
Combined aqueous layers
Ether layer
Extract with ether
Aqueous layer discarded.
Ether layer.
Wash with water until free from soaps
Aqueous layer discarded
Ether layer
Evaporate spontaneously in room
Recrystallize residue from ether at room temperature until free from lipochrome
Dissolve in ether, saponify with sodium ethylate, filter, wash with ether
On filter soaps discarded
Filtrate and ethereal washings
Dilute with ether, wash with water several times
Aqueous layers combine and extract with ether
Ether layer
Aqueous layer discarded
Ether layer
Evaporate before electric fan
Dissolve residue in ether, saponify with sodium ethylate, filter out soaps, wash with ether
On filter soaps discarded
Filtrate and ethereal washings
Dilute with ether, wash with water until free from soaps
Aqueous layers combine and extract with ether
Ether layer
Aqueous layer discarded
Ether layer
Wash free from soaps with water
Aqueous layer discarded
Ether layer
Evaporate before electric fan
Recrystallize residue from ether at room temperature until free from lipochrome

Alcoholic Potash"), until at last crystals free from lipochrome were obtained.

The two methods are outlined in Table III.

A set of three preparations of cholesterol from brain was thus obtained from the first, second, and third ether extracts, respectively, by means of saponification with boiling alcoholic potash; another set of three preparations was obtained from these three ether extracts by means of saponification with sodium ethylate at the temperature of the room. The filtrates and washings from all six of these preparations were combined. After the evaporation of the ether, a voluminous precipitate of cholesterol deposited, which was removed from the supernatant alcohol by filtration, washed with a small quantity of alcohol, and recrystallized from ether, in the manner already described, until the crystals were entirely free from lipochrome. (G, Table IV.)

The melting-point of each preparation was determined by means of thermometers, certified by the United States Bureau of Standards, and was corrected by the formula of Bömer:[21]

S—Corrected melting-point.

T—Observed melting-point.

t—Mean temperature of the air, surrounding the projecting mercury column, ascertained by means of a second thermometer, which records the temperature of that column at a point midway between the surface of the liquid in the bath and the point *T* of the first thermometer.

n—The length, in thermometer degrees, of the column of mercury of the first thermometer projecting above the surface of the bath.

$$S = T + 0.000154n\ (T-t).$$

The melting-points of the samples of cholesterol obtained from brains, as well as of those obtained from gall-stones, are given in Table IV. For purposes of comparison, the melting-points of certain mixtures of these preparations are also included in that table. The results will be discussed after a description has been given of the preparation of cholesterol from gall-stones (H and I, Table IV).

Cholesterol from Gall-Stones.

Twelve grammes of gall-stones, varying in size from that of a grain of rice to that of a shell-bark, were obtained from human cadavers, and were ground to a fine powder in a mortar. The

powder, which possessed a reddish-brown color, was extracted with 300 c.c. of absolute ether at the temperature of the room, shaking at intervals, for a period of twelve days. The ethereal solution was poured through a filter and the residue of bile-pigments was washed with absolute ether. The filtrate and washings were combined and permitted to evaporate spontaneously at room temperature from a crystallizing dish which was covered with a watch-glass. The major portion of the cholesterol deposited on the sides of the dish as a mass of needles, pearly-white in color, save at the top, where a yellow rim appeared; a scanty yellowish deposit also formed on the bottom

TABLE IV.

MELTING-POINTS OF PREPARATIONS OF PURE CHOLESTEROL AND OF MIXTURES OF THESE PREPARATIONS.

Sample	Source	Mode of saponification	Number of crystallizations	Quantity obtained, grammes	Corrected melting-point °C.	Crystal form
A	Brain, first extract	Alcoholic potash	2	9.4	149.1	Plates
B	Brain, second extract	Alcoholic potash	2	4.5	148.5	Plates
C	Brain, third extract	Alcoholic potash	2	3.5	149.0	Plates
D	Brain, first extract	Sodium ethylate	3	8.2	149.1	Needles
E	Brain, second extract	Sodium ethylate	3	6.5	148.7	Plates
F	Brain, third extract	Sodium ethylate	4	2.9	148.4	Needles
G	Brain, mother liquors of A to F	.....	2	6.7	147.1	Needles
H	Gall-stones	.....	1	5.4	147.4	Needles
I	Gall-stones	.....	2	4.3	147.4	Plates
A plus C, 50 per cent. of each	.....	.....	.	...	147.8	.....
D plus F, 50 per cent. of each	.....	.....	.	...	147.7	.....
A plus D, 50 per cent. of each	.....	.....	.	...	148.0	.....
A plus H, 50 per cent. of each	.....	.....	.	...	147.8	.....

of the dish. The yellow portion was removed from the deposit on the sides of the dish by means of a scalpel, and the pure white material was preserved as sample H. The yellow portion was combined with the deposit on the bottom of the dish, and then recrystallized from absolute ether plus a few cubic centimetres of alcohol until free from lipochrome, in the manner already described in the preparation of cholesterol from brain; sample I was thus obtained.

DISCUSSION OF THE RESULTS.

Upon reference to Table IV it is seen that the melting-point of all six of the samples prepared from brain—A to F, inclusive—is practically the same; the difference between the extreme values is but 0.7° C. From this fact the conclusions are naturally drawn: The cholesterol obtained from the first, from the second, and from the third extract of brain is one and the same chemical individual, free from any contaminating body, for any contaminant would have accumulated in either the first or the third extract, and demonstrated its presence by its influence on the melting-point. The heating during the process of saponification with boiling alcoholic potash does not produce any rearrangement of the molecule of cholesterol, for if such a change occurred the melting-point of the compound obtained by saponification with alcoholic potash would differ from that of the compound obtained by saponification with sodium ethylate at a temperature never exceeding that of the body.

As might be expected, the melting-point of the cholesterol, sample G prepared from the mother liquors, was somewhat lower than that of the other six samples, for any compounds which had accompanied the cholesterol from the brain and had passed into the mother liquors would tend to contaminate the cholesterol derived from those liquors and to depress its melting-point.

The cholesterol from gall-stones melted at a slightly lower temperature than did the first six samples from brain, yet the figures lie so close that they bear witness to the identity of the cholesterol from the two sources. Moreover, the melting-point of the material from gall-stones lies above that of the cholesterol G, from the mother liquors of the brain preparations.

The melting-points of the mixtures also command attention. Equal quantities by weight of two samples were ground intimately in a mortar, and the melting-point of the mixture was determined. When two masses have the same melting-point, and are mixed intimately in equal proportions by weight, if the two masses are the same chemical individual in a state of purity the melting-point of this mixture will vary but slightly, if at all, from that of either of the mixed masses. However, if the two mixed masses are different chemical compounds, by the law of Raoult the melting-point of this mixture will be far below that of either of the two constituent masses. The melting-points of the mixture of samples A and C and of the mixture of samples D and F bear witness that the cholesterol of the first and of the third extract—and therefore, by inference, of the second extract—is one and the same chemical individual. The melting-point of the mixture of samples A and D again shows that no rearrangement of the cholesterol molecule is brought about by the heat during the saponification with alcoholic potash, and that both modes of saponification yield the same cholesterol. The melting-point of the mixture of samples A and H proves the identity of cholesterol from brain and that from gall-stones.

Lastly, the melting-point of the mixture of samples A and H, combined with the fact that the melting-points of the samples prepared from gall-stones lie so very close to the melting-points of the samples prepared from brain, gives evidence that neither potassium hydroxide nor sodium ethylate gives rise to a rearrangement of the cholesterol molecule. The cholesterol from gall-stones was never in contact with either of these alkaline reagents, yet it is exactly the same chemical compound as the cholesterol from brain in the preparation of which one of these two reagents was always used.

To sum up, the data for melting-points demonstrate the uniform purity of all the samples of cholesterol and also prove that all these samples are one and the same chemical compound.

For purposes of comparison, it may be mentioned that, according to Bömer,[21] the corrected melting-point of cholesterol lies between 148.4° and 150.8° C., while Polenske [90] has determined the corrected melting-point of 254 samples of cholesterol from lard with the following results:

Number of samples	Corrected melting-point, °C.
2	145
15	146 –146.5
36	146.5–147
185	147 –148
15	148
1	148.5

III. CHOLESTEROL AND THE IODINE REAGENTS FOR FAT ANALYSIS.

In the course of the introduction to this dissertation certain reactions were discussed which demonstrate the presence of at least one, and possibly of two double bonds, in the molecule of cholesterol. The addition compounds of cholesterol, including those with halogens and haloid acid, were described. Certain of these compounds have found application in the analytical chemistry of cholesterol. Thus von Bondzynski and Humnicki [44] devised a method for the separation of cholesterol and coprosterol, which depends on the fact that cholesterol is converted by bromide into cholesterol dibromide, a compound insoluble in petroleum ether, while coprosterol is not acted on by bromine and is readily soluble in petroleum ether. Windaus [83] has separated cholesterol and phytosterol by means of the difference in solubility of their dibromides in ice-cold glacial acetic acid, which dissolves phytosterol dibromide, while cholesterol dibromide is insoluble.

The iodine number of cholesterol has also been determined. Lewkowitsch [14] obtained 68.09 and 67.3 by the method of Hübl; Marcusson [84] obtained 29.4 by the method of Waller and 109.4 by the method of Wijs.

For the determination of the iodine number, which is a measure of the unsaturated or double bonds, four methods exist—those of Hübl,[85] Wijs,[86] Hanus,[87] and Waller.[88] The last method is comparatively unimportant. Hübl used a solution of iodine plus mercuric chloride in 95 per cent. alcohol. Waller added 5 per cent. of hydrochloric acid of specific gravity 1.19 to this solution, and also used as a solvent alcohol into which hydrogen chloride had been passed. The reagent of Wijs was a solution of iodine monochloride in 95 per cent. acetic acid; that of Hanus a solution of iodine monobromide in glacial acetic acid. In this research the reagents of Hübl and Hanus were

prepared and used as directed by the Association of Official Agricultural Chemists;[89] the reagent of Wijs contained iodine monochloride in exactly the same molecular concentration as that of iodine monobromide in the reagent of Hanus. Ten cubic centimetres of chloroform were always used as a solvent for the cholesterol. The 0.1 normal sodium thiosulphate, for titration of the unabsorbed iodine, was standardized against potassium permanganate which had just been checked with ferrous ammonium sulphate. The results obtained by these three methods are collected in Table V. For a full description of each sample of cholesterol, reference should be made to Table IV.

TABLE V.

IODINE NUMBER OF CHOLESTEROL.

Experiment number	Sample of cholesterol	Weight of cholesterol	Iodine number	Volume of iodine reagent	Name of iodine reagent	Period of absorption
1	D	0.1010	74.4	25		
2	D	0.1021	74.8	25		
3	D	0.2494	70.8	25		
4	D	0.2537	70.3	25		
5	I	0.2518	71.3	25		
6	I	0.2564	71.6	25		
7	H	0.2603	71.3	25	Hübl...	17 hours
8	H	0.2683	71.3	25		
9	H	0.2530	74.6	25		
10	D	0.5006	78.0	50		
11	D	0.5027	77.9	50		
12	I	0.1013	81.1	25		
13	I	0.1036	79.3	25		
14	H	0.2464	74.0	25	Hanus..	30 minutes
15	I	0.6451	71.4	50		
16	I	0.1269	144.7	25		
17	D	0.2501	106.0	25		
18	D	0.2516	100.3	25		
19	D	0.2506	154.2	50	Wijs....	30 minutes
20	D	0.2529	158.9	50		
21	D	0.5006	56.4	25		
22	D	0.5036	55.1	25		

The iodine number of cholesterol is 65.7. This figure is based on the formula $C_{27}H_{46}O$, the presence of one double bond in the molecule, and the atomic weights H = 1.008; C = 12.00; O = 16.00; I = 126.92. The values obtained in this research are all higher than the theoretical value, save in experiments 21 and 22 by the Wijs method. The Hübl method tended to give

the lowest values; although even in experiments 10 and 11, where the conditions were as prescribed by Lewkowitsch [14] (0.5 to 0.6 gramme cholesterol, 50 c.c. chloroform, and 25 c.c. of *each* solution or 50 c.c. of the mixed reagent of Hübl), the iodine number is too high. In the Hanus method the tendency is toward still higher results, while the highest values of all are obtained by the use of the Wijs method. Thus the iodine numbers obtained in experiments 16, 19, and 20 are over twice the theoretical value. There is a marked tendency, especially apparent in the case of the Hanus and Wijs methods, for the iodine number to become higher, the greater the excess of the iodine reagent. These phenomena might be explained by the saturation of a second double bond or, possibly, by the breaking of an intracyclic bond or bridge; however, in such a case the iodine number would be a simple multiple of 65.7, and the results obtained are not simple multiples of that figure. The explanation of these results must therefore be sought in another direction—possibly saturation of the one double bond is followed by direct substitution of halogen. The iodine numbers here obtained demonstrate that cholesterol cannot be determined volumetrically by means of the iodine reagents of fat analysis.

IV. METHODS FOR THE QUANTITATIVE DETERMINATION OF CHOLESTEROL.

GRAVIMETRIC DETERMINATION AS FREE CHOLESTEROL.

In the gravimetric methods for the quantitative determination of cholesterol the latter is weighed as the free alcohol, as cholesteryl benzoate or as digitonin cholesteride. Ritter [91] has made an exhaustive study of the extraction and determination, gravimetrically, of cholesterol as the free alcohol. He recommends that 50 grammes of fat be dissolved in 100 c.c. of boiling alcohol in a porcelain dish of 1500 c.c. capacity; 8 grammes of metallic sodium are dissolved in 160 c.c. of 99 per cent. alcohol, and the hot solution of sodium ethylate is immediately added to the boiling alcoholic solution of the fat; the mixture is well stirred and is evaporated until the alcohol has been completely removed. Sodium chloride, in weight one and one-half times that of the fat, is added, and, in order to insure an intimate mixture of the soaps and salt, the latter are almost, if not entirely, dissolved in

water. The solution is evaporated with frequent stirring, over a free flame, until crystallization begins, then on the water-bath until dry. The dish and its contents are then further dried in an oven at 80° C., and the process of pulverizing the residue in the dish is begun as soon as the latter is sufficiently dry. A fine powder is finally obtained, which is dried in a desiccator over sulphuric acid, then is extracted with ether in a Soxhlet apparatus for a period of nine hours. The ether extract is then poured into an Erlenmeyer flask of 750 to 1000 c.c. capacity, and the extraction flask is washed with several successive portions of ether, which are also poured into the Erlenmeyer flask. The ether is evaporated; the residue is dissolved in a very small quantity of alcohol on the water-bath, and water is gradually added, agitating the flask meanwhile, until it is almost full. The precipitated cholesterol is collected on a filter and washed with water. The filter and its contents are dried at 60° C., the cholesterol is transferred, as far as possible, to a tared flask; the filter is washed with ether to remove the last traces of cholesterol, and these washings are received in the tared flask. The ether is evaporated, and the residue is completely dried at 100–120° C., then weighed. According to Ritter, the sodium chloride gives porosity to the dry mass, prevents the solution of the soaps in ether, and also has another specific action in assisting the solution of the cholesterol in the ether. The nature of this specific action, which is not exerted by sand or paper, Ritter states cannot be explained with certainty. Corper[92] found that the presence of an excess of sodium ethylate in the mixture of soaps and salt prevents the quantitative extraction of the cholesterol by the ether. In a second paper Corper[93] states that this error may be eliminated by passing a current of carbon dioxide gas through the aqueous solution of the soaps for a period of three to five hours in order to decompose the excess of ethylate. The salt is then added and the procedure carried out as outlined above.

Cappenberg[94] has devised the following method for the isolation and gravimetric determination of cholesterol as the free alcohol. The ether extract of the crude material is saponified with alcoholic potash, the soap solution is evaporated to complete dryness, and the residue is ground and extracted with absolute ether. The ethereal solution is filtered; the ether is

evaporated and the residue is dissolved in hot methyl alcohol. Twenty per cent. of water is added to the hot solution, which is then concentrated until crystallization of the cholesterol begins. The solution is then cooled to 0° C., whereupon all the cholesterol separates as crystals, which are at once collected on a tared filter and washed first with 50 per cent. methyl alcohol, then with hot water. The filter and its contents are dried at 100° C. to constant weight.

Usually cholesterol is determined in a fat or in the ether extract of a tissue, excrement, or food. Grigaut[95] uses tissue itself. He directs that 20 to 40 c.c. of blood-serum or 2 to 10 grammes of freshly-ground tissue be mixed with 60 to 80 c.c. of a 20 per cent. aqueous soda solution in a flask, which is closed with a cotton plug. The flask and its contents are heated for one hour at 110° C. in an autoclave. After cooling, the aqueous solution is transferred to a separatory funnel and shaken with one or two volumes of common ether. The extraction with ether is repeated, the two ether extracts are combined, and the solvent is evaporated. The residue is dissolved in a small quantity of alcohol; 1 c.c. of alcoholic soda is added; the solution is evaporated to dryness, and the residue is kept in an oven at 100° C. for 30 minutes. While the dish is still warm, the residue is dissolved in petroleum ether; the solution is filtered and the filter is washed with petroleum ether. The combined filtrate and washings are evaporated, and the residue of cholesterol is dried at 100° C. to constant weight.

GRAVIMETRIC DETERMINATION AS CHOLESTERYL BENZOATE.

The gravimetric determination of cholesterol as cholesteryl benzoate has been described by Dorée and Gardner[20]. They direct that 1 gramme of the unsaponifiable portion of the ether extract be dissolved in 10 to 20 c.c. of pyridine. A slight excess of benzoyl chloride, dissolved in pyridine, is added, and the solution is allowed to stand for several hours, then poured into water. The precipitated cholesteryl benzoate is recrystallized from absolute alcohol. According to Gardner,[96] at 20° C. each 100 c.c. of the mother liquor retains 0.12 gramme of the ester. The crystals are more difficultly soluble; after standing in alcohol for several hours at 20° C., with occasional shaking, only 0.029 gramme of the crystalline benzoate had dissolved in each 100 c.c. of solvent.

GRAVIMETRIC DETERMINATION AS DIGITONIN CHOLESTERIDE.

The preceding methods have been available for the determination of *total* cholesterol only. The digitonin cholesteride method of Windaus[62] permits the determination of free, esterified, and total cholesterol. Free cholesterol combines with the glucoside digitonin (digitin, digitalin) to form digitonin cholesteride. One molecule of cholesterol $C_{27}H_{46}O$ unites with one molecule of digitonin $C_{55}H_{94}O_{28}$ without elimination of water to form the cholesteride $C_{82}H_{140}O_{29}$. The cholesterol should be dissolved in fifty-fold its quantity of boiling 95 per cent. alcohol; the digitonin should be a 1 per cent. solution in hot 90 per cent. alcohol; when the hot solutions are mixed, the digitonin cholesteride is precipitated. The weight of the cholesteride, after drying at 100° C., is multiplied by the factor 0.2431 in order to obtain the weight of cholesterol contained in it. The esters of cholesterol do not react with digitonin, but remain in solution. Windaus studied the cholesterol content of kidneys. The ether extract of these organs was treated with thirty-fold its quantity of boiling 95 per cent. alcohol. Whenever the extract was not completely soluble in the alcohol, it was boiled with several successive portions of that solvent in order to completely remove free cholesterol, which was then determined in the combined alcoholic solutions. The solution of digitonin was added as long as a precipitate formed. After having stood for several hours in order to permit the precipitate to settle, the supernatant liquid was tested with digitonin solution to make sure that all the free cholesterol had been precipitated. The precipitate was collected on a Gooch crucible, washed with alcohol and ether, dried at 100° C., and weighed. The quantity of free cholesterol was then calculated.

That portion of the original ether extract of the kidney which was insoluble in alcohol was dissolved in a mixture of alcohol and ether, and was combined with the filtrate and washings from the determination of free cholesterol. The alcohol-ether solution was concentrated, diluted with water, and extracted with ether or petroleum ether, which dissolved out the lipins, including the cholesteryl esters. The ether was evaporated; the residue was saponified by means of hot sodium ethylate in order to liberate the cholesterol from its esters; the

cholesterol was extracted from the solution with petroleum ether, and was finally precipitated and weighed as digitonin cholesteride. The quantity of esterified cholesterol was then calculated. The total cholesterol was the sum of the free and esterified cholesterol.

VOLUMETRIC METHODS.

The volumetric methods which have been suggested for the determination of cholesterol are:

(*a*) Determination of the iodine number.

(*b*) Determination of the acetyl saponification number.

(*c*) Titration with bromine.

Lewkowitsch [14] recommended the use of the iodine number, as determined by Hübl's method, for the volumetric estimation of cholesterol. However, since the iodine number of cholesterol varies between wide limits and is always abnormally high, as was shown in Part III of this dissertation, this method is not quantitative.

Lewkowitsch [14] by experiment obtained 137.4 and 132.4 as the acetyl saponification number of cholesterol (the saponification number of cholesteryl acetate), while the theoretic value was 135.5. He therefore recommended the determination of this constant as an admirable method for the estimation of cholesterol, as such, in mixtures with other lipins which do not influence the reaction.

According to Nukada,[97] the true acetyl value (which is a measure of hydroxyl groups) of the fat of man, swine, sheep, geese, and of their insoluble fatty acids, cannot be taken as a measure of the quantity of free and total cholesterol respectively, for the values are far too high to check with determinations of unsaponifiable matter, and are influenced by the hydroxy acids of the fat.

Obermüller [98] determined the cholesterol content of the unsaponifiable matter of a fat or oil by titration with bromine. The unsaponifiable matter was dissolved in a few cubic centimetres of carbon disulphide, and a 2.97 per cent. solution of bromine in carbon disulphide was added from a burette until a distinct change in color from yellow to yellowish-red occurred. Chloroform cannot be used as the solvent.

COLORIMETRIC METHODS.

The methods for the colorimetric determination of cholesterol are based on the reactions of Salkowski[99] and Liebermann.[100] Schulze[101] has used these reactions in the colorimetric determination of phytosterol. The colorimetric determination of total cholesterol by means of Liebermann's reaction has been studied by Grigaut.[102] He recommends that 2 c.c. of blood-serum or 0.1 to 1.0 gramme of freshly-ground tissue be heated on a water-bath for 5 to 20 minutes with 20 c.c. of 1 per cent. solution of soda in 50 per cent. alcohol. After cooling, the solution is extracted, first with 50 c.c. of ether, then with 30 c.c. of the same solvent. The combined ether extracts are washed with water; the ether is evaporated; the residue is dissolved in 5 c.c. of chloroform; 2 c.c. of pure acetic anhydride are added, followed by 2 drops of concentrated sulphuric acid. The color is permitted to develop. In one-half hour it passes through red, blue, bluish-green, to a beautiful green, which persists for one hour. At the same time, a standard is prepared by treating 5 c.c. of a solution of 0.06 gramme of cholesterol in 100 c.c. of chloroform with acetic anhydride and concentrated sulphuric acid as just described. Should the color of the standard not match that of the determination proper, the more intensely colored solution is diluted with a mixture of chloroform, acetic anhydride, and concentrated sulphuric acid, which contains these reagents in the proportions already indicated, until the colors are of the same intensity. The quantity of cholesterol in the unknown is then calculated. The results obtained by this colorimetric method may differ by one-fifteenth from the results obtained by Grigaut's gravimetric method,[95] which gives the higher figures.

Weston[103] and Weston and Kent[37] have applied the Salkowski reaction for the colorimetric determination of total cholesterol in blood analysis. According to these investigators, the presence of less than two milligrammes of cholesterol in one cubic centimetre of chloroform gives rise to the following phenomena in Salkowski's reaction. Both the chloroform solution and the sulphuric acid rapidly pass through a yellowish-green to an amber color, which remains unchanged for about an hour, then becomes pink, and finally violet. However, after the

mixture has stood for 15 to 30 minutes, the addition of a small quantity of chloroform causes the amber color to disappear, and, in a few minutes, the colorless solution begins to show the pink tint which is characteristic of cholesterol. The crude cholesterol, obtained from 2.5 c.c. of serum as described below, is dissolved in 5 c.c. of chloroform, and 0.15, 0.2 and 0.25 c.c. of this solution are diluted to a volume of 1 c.c. each with chloroform. Nine standard solutions of cholesterol are prepared by diluting with chloroform a solution of 0.5 gramme of cholesterol in 50 c.c. of that solvent, so that 1 c.c. of the standards represents 0.0001, 0.000125, 0.00015, 0.000175, 0.0002, 0.000225, 0.00025, 0.000275, and 0.0003 gramme of cholesterol, respectively. One cubic centimetre of each dilution of the unknown and of each standard is placed in a separate tube, the dimensions of which are 1 cm. by 10 cm.; 0.1 c.c. of sulphuric acid (1.81 sp. gr.) is added to each tube, which is then shaken twenty times and permitted to stand for 30 minutes. At the end of that period of time, 1 c.c. of chloroform is added to each tube without disturbing the sulphuric acid. The tubes are placed in the dark for 15 minutes. As soon as the series of standards shows a gradation of color from barely perceptible pink to deep pink, they are compared with the unknowns and the cholesterol content of the latter is calculated. The comparison is made by looking through the tubes, while holding them against a white surface. The color of the unknown should lie near or slightly below the middle of the scale of standards. The chloroform used must be of a high degree of purity. The extraction of the crude cholesterol from serum may be outlined. The 2.5 c.c. of serum are treated successively with alcohol at 60° C., ether, and boiling alcohol. The alcohol and ether solutions are combined and saponified with sodium hydroxide, then treated with calcium hydroxide solution, which produces a precipitate containing all the cholesterol. The dried precipitate is extracted with several portions of ether in order to recover the cholesterol; the ether is evaporated and the residue is used for the colorimetric estimation of cholesterol.

STUDY OF THE GRAVIMETRIC METHODS.

In the following experiments the gravimetric determination of cholesterol as the free alcohol, as cholesteryl benzoate, and as digitonin cholesteride was studied.

Determination of Cholesterol as the Free Alcohol.

Cappenberg's Method (Table VI).—In order to learn the influence of the crystallization from methyl alcohol on the quantitative yield of cholesterol, experiments 23 and 24 were carried out. The cholesterol was dissolved in 15 c.c. of hot methyl alcohol; the solution was concentrated to a volume of 10 c.c., and 2 c.c. (20 per cent.) of water were added, whereupon crystals of cholesterol separated. The solution was permitted to cool to the temperature of the room, and was further cooled by packing in ice and salt for a period of five to fifteen minutes. The cold supernatant liquid was poured into a tared Gooch crucible; the precipitate of cholesterol was transferred to the crucible, and was washed with 20 c.c. of ice-cold 50 per cent. methyl alcohol, then with 50 to 75 c.c. of hot water. The crucible and its contents were dried for two hours at 100–110° C., permitted to cool in a desiccator over calcium chloride, and weighed. The filtrate and the alcoholic washings were perfectly clear, but the dilution with the aqueous washings gave rise to a slight opalescence. The results show that a loss of cholesterol occurred during the crystallization.

TABLE VI.

DETERMINATION OF CHOLESTEROL BY THE METHOD OF CAPPENBERG.

Experiment number	Sample	Weight of cholesterol taken	Weight of cholesterol found	Per cent. of cholesterol recovered
23	H	0.2089	0.2049	98.09
24	H	0.2010	0.1982	98.61
25	H	0.2099	0.1983	94.47
26	H	0.2042	0.1927	94.37

The complete procedure of Cappenberg was carried out in experiments 25 and 26. The cholesterol was heated on the water-bath for thirty minutes with 50 c.c. of alcoholic potash, and the solution was then evaporated to complete dryness. The residue was ground and extracted with absolute ether; the ethereal solution was filtered; the filter was washed with ether, and the combined filtrate and washings were evaporated to dryness on the water-bath. The residue of cholesterol was subjected to crystallization from methyl alcohol, as was described in detail

for the preceding set of experiments. The dilute methyl alcohol and the water which were used for washing the cholesterol ran through the Gooch crucible rather slowly.

When the results of the two sets of experiments were compared it was seen that, during the complete procedure of saponification, extraction and crystallization (experiments 25 and 26), a greater loss of cholesterol occurs than takes place during the process of crystallization alone (experiments 23 and 24).

Ritter's Method (Table VII).—Two experiments (27 and 28) were carried out as directed by Corper.[93] The cholesterol was dissolved in 10 c.c. of absolute alcohol—in a large beaker—with the aid of heat. Forty cubic centimetres of an alcoholic solution of sodium ethylate (5 grammes of sodium dissolved in 100 c.c. of absolute alcohol) were added, and the solution was heated on a water-bath for twenty minutes, then permitted to stand over night. One hundred cubic centimetres of water were added, and a slow current of carbon dioxide was passed for five consecutive hours through the resulting suspension of cholesterol. The gas was generated in a Kipp apparatus by the action of hydrochloric acid on marble, and was washed by passing through a solution of sodium bicarbonate. The suspension was heated and transferred quantitatively to a casserole; 30 grammes of sodium chloride were added and the solution was evaporated to complete dryness by prolonged heating on the water-bath. The residue was ground in a mortar, transferred to a fat-free paper thimble, dried in the oven at 100–110° C., and extracted for nine hours with absolute ether in a Soxhlet extractor.

The ether was transferred to a separatory funnel; the extraction flask was washed several times with ether and the washings were added to the ethereal extract. The ethereal solution was washed three times with water, then transferred to a small tared flask. The combined wash waters were shaken with ether to recover any cholesterol in them; the ether was washed twice with water, and then transferred to the tared flask containing the ethereal solution. The ether was evaporated on the water-bath and the flask was dried for two hours at 100–110° C. and weighed. Corper states that this method is "accurate within milligrammes."

The treatment with carbon dioxide requires several hours. In order to shorten the period of time required for the neutraliza-

tion of the excess of sodium ethylate, three experiments—29 to 31, inclusive—were carried out as outlined above, but, instead of treatment with carbon dioxide, the aqueous-alcoholic suspension of cholesterol was neutralized with 2/N hydrochloric acid solution, using phenolphthalein as the indicator. In addition to the sodium chloride, 2 grammes of sodium bicarbonate were added in order to insure the presence of sodium carbonate in the dried residue after evaporation.

When carbon dioxide was used, good duplicates were not obtained, although the cholesterol used in the two experiments was from the same source and had the same melting-point. When hydrochloric acid was used, two of the results were excellent duplicates, but the third result was far too low. The values obtained after the use of hydrochloric acid are lower than those obtained after the use of carbon dioxide. The method, on the whole, tends to give lower results than does the method of Cappenberg.

TABLE VII.

DETERMINATION OF CHOLESTEROL BY MODIFICATIONS OF RITTER'S METHOD.

Experiment number	Sample	Weight of cholesterol taken	Weight of cholesterol found	Per cent. of cholesterol	Acid used for neutralization
27	H	0.1038	0.1037	99.90	Carbon dioxide
28	I	0.1043	0.0964	92.43	
29	H	0.1046	0.0673	64.34	Hydrochloric acid
30	H	0.1037	0.0924	89.10	
31	I	0.1018	0.0907	89.10	

Determination of Cholesterol as Cholesterol Benzoate.

The cholesterol was dissolved in 5 to 10 c.c. of pyridine, and a solution of 0.5 c.c. of benzoyl chloride in 5 c.c. of pyridine was added. The resulting solution was well mixed and permitted to stand over night at the temperature of the room, then was poured into water. In experiments 32 to 35, inclusive, 80 to 100 c.c. of water were used; in experiments 36 to 38, inclusive, 500 c.c. of water were used. On stirring, a white flocculent precipitate of cholesteryl benzoate separated, which at first floated, then settled to the bottom of the beaker. The supernatant liquid was somewhat opalescent. The precipitate was collected on a

smooth, hardened filter-paper; the filtrate was perfectly clear, and its chloroform extract gave a negative reaction with Salkowski's reagent, hence contained no cholesterol. The precipitate was washed with a few cubic centimetres—5 to 7—of cold alcohol, and was then recrystallized from alcohol.

The directions of Gardner [96] are rather indefinite as to the strength of the alcohol to be used for this purpose. He states that cholesteryl benzoate "is only slightly soluble in absolute alcohol. If recrystallized from alcohol, the mother liquors retain at 20° 0.12 gramme per 100 c.c. The crystals are, however, more difficultly soluble. The writer found that on allowing crystals to stand in alcohol at 20° for several hours with occasional shaking only 0.029 gramme dissolved in 100 c.c." He also directs that the recrystallized cholesteryl benzoate be weighed, "in which case a correction may be made for the solubility in alcohol."

Absolute alcohol was used throughout experiments 32 to 36, inclusive; 95 per cent. alcohol was used in experiments 37 and 38. The filter and precipitate were boiled with several successive portions of alcohol, the hot solution of cholesteryl benzoate was filtered, and the filter washed with hot alcohol. The combined filtrate and washings were concentrated to a volume of approximately 20 c.c., then permitted to stand over night at the temperature of the room. The precipitate of cholesteryl benzoate was collected on a tared Gooch crucible and sucked free from mother liquor, the volume of which was then measured. The precipitate was next washed with a known volume of alcohol, dried for two hours at 100–110° C., and weighed.

Table VIII presents data for the volume of mother liquor, the cholesteryl benzoate content of which has been calculated in grammes by multiplying the volume in cubic centimetres by the factor 0.0012. In that table the volume of wash alcohol is also given; its content of cholesteryl benzoate in grammes has been obtained by multiplying the volume in cubic centimetres by the factor 0.00029. The sum of the weight of crystalline cholesteryl benzoate plus that of the ester contained in the mother liquor and in the washings is the "Total weight of cholesteryl benzoate," from which the corresponding weight of cholesterol has been calculated.

When 95 per cent. alcohol was used for recrystallization

TABLE VIII.

DETERMINATION OF CHOLESTEROL AS CHOLESTERYL BENZOATE.

Experiment number	Sample	Weight of cholesterol taken	Weight of cholesteryl benzoate crystals	Volume of mother liquor, c.c.	Volume of wash alcohol, c.c.	Weight of cholesteryl benzoate in mother liquor	Weight of cholesteryl benzoate in wash alcohol	Total weight of cholesteryl benzoate	Weight of cholesterol corresponding to weight of total benzoate	Per cent. of cholesterol recovered
32	H	0.5119	0.2591	14.5	20.0	0.0174	0.0058	0.2823	0.2224	43.45
33	H	0.5076	0.1668	18.7	20.0	0.0224	0.0058	0.1950	0.1536	30.26
34	H	0.5008	0.1745	10.8	20.0	0.0130	0.0058	0.1933	0.1523	30.41
35	H	0.5174	0.1410	10.7	20.0	0.0128	0.0058	0.1596	0.1257	24.29
36	H	0.5142	0.3078	12.8	20.0	0.0154	0.0058	0.3290	0.2592	50.41
37	D	0.5077	0.3723	15.5	25.2	0.0186	0.0073	0.3982	0.3137	61.79
38	D	0.5060	0.3503	19.4	27.6	0.0233	0.0080	0.3816	0.3006	59.41

(experiments 37 and 38), the per cent. of cholesterol recovered was somewhat higher than in any of the other experiments, where absolute alcohol was used. However, in no case was even two-thirds of the weight of cholesterol taken recovered. The least amount recovered was 24.29 per cent., the greatest 61.79 per cent., the average of the seven experiments 42.86 per cent. This method, therefore, is not quantitative. Since no cholesterol was present in the aqueous filtrate from the precipitate of cholesteryl benzoate, and since that precipitate was completely dissolved in the boiling alcohol, the cholesterol not recovered must have remained in the alcoholic mother liquors, and the solubility of cholesteryl benzoate in alcohol must be greater than the values recorded in the literature. However, since from one-third to three-fourths of the cholesterol taken was not recovered, a redetermination of the solubility of the ester in alcohol and new correction factors based thereon would not render the determination of cholesterol as cholesteryl benzoate a suitable method for gravimetric analysis.

Determination of Cholesterol as Digitonin Cholesteride.

The cholesterol was dissolved in 10 c.c. of 95 per cent. alcohol; to this boiling solution was added an excess of a boiling 1 per cent. solution of digitonin in 90 per cent. alcohol. One part by weight of cholesterol combines with slightly more than three parts by weight of digitonin. In order to insure the presence of an excess of the latter, four parts by weight of digitonin were always used for one part by weight of cholesterol. After the two boiling solutions had been mixed, the resulting mixture was permitted to stand over night at room temperature. Precipitation of digitonin cholesteride usually began in the boiling solution and was completed on standing. The precipitate was collected on a tared Gooch crucible, washed with 95 per cent. alcohol and ether, dried for two hours at 100–110° C., and weighed. The cholesterol content of the precipitate was calculated by multiplying the weight of the latter by the factor 0.2431. The filtrate and washings ran through the Gooch crucible rather slowly. When the digitonin was dissolved in absolute alcohol, it produced no precipitate in solutions of cholesterol in 95 per cent. alcohol; however, after sufficient water had been added to the mixture to reduce the strength of the alcohol derived from

the digitonin solution to 90 per cent., the precipitate formed quantitatively.

The results obtained by this method are given in Table IX. The least proportion of cholesterol recovered was 93.63 per cent., the greatest 103.02 per cent.; the average of ten experiments was 97.37 per cent.

TABLE IX.

DETERMINATION OF CHOLESTEROL AS DIGITONIN CHOLESTERIDE.

Experiment number	Sample	Weight of cholesterol taken	Weight of digitonin cholesteride	Weight of cholesterol found	Per cent. of cholesterol recovered
39	A	0.0511	0.2039	0.0496	97.06
40	B	0.0501	0.1995	0.0485	96.81
41	C	0.0511	0.2081	0.0506	99.02
42	D	0.0496	0.2101	0.0511	103.02
43	E	0.0502	0.1932	0.0470	93.63
44	F	0.0523	0.2168	0.0527	100.76
45	I	0.0498	0.1953	0.0475	95.38
46	I	0.0512	0.2022	0.0492	96.09
47	I	0.1468	0.5787	0.1407	95.84
48	I	0.1521	0.6015	0.1462	96.12

Comparison of the Gravimetric Methods.

The gravimetric determination of cholesterol as the free alcohol, as cholesteryl benzoate, and as digitonin cholesteride has been studied in the course of this research.

Of the methods for the determination as the free alcohol, that of Cappenberg (Table VI) is preferable to the modified Ritter method (Table VII). By Cappenberg's procedure excellent duplicates were obtained; while in the Ritter methods unsatisfactory duplicates were the rule when carbon dioxide was used, and the results were too low when hydrochloric acid was used.

The determination of cholesterol as cholesteryl benzoate (Table VIII) is not a quantitative method.

The determination of cholesterol as digitonin cholesteride (Table IX) is the best method of all. It is the most accurate, surpassing even Cappenberg's method in this respect, and, moreover, is by far neater and less complicated than the latter.

V. CONCLUSIONS.

Cholesterol, extracted from brain, has been purified by saponification either with sodium ethylate at room temperature or with

boiling alcoholic potash, in each case followed by crystallization from ether. Cholesterol has also been prepared from gall-stones by extraction with ether and crystallization from that solvent.

The melting-points of the six samples from brain, 148.4–149.1° C.; of the two samples from gall-stones, 147.4° C., and of various mixtures of two samples (50 per cent. of each sample), 147.7–148.0° C., demonstrate the identity of the cholesterol from the two sources.

The melting-points of the samples and of their mixtures also show that neither heat in the process of saponification, nor alkaline reagents such as alcoholic potash and sodium ethylate, produce any rearrangement in the molecule of cholesterol.

The iodine reagents of fat analysis cannot be used for the volumetric determination of cholesterol. The iodine number of pure cholesterol has been determined by the methods of Hübl, Hanus, and Wijs. The Hübl method tended to give the lowest values, 70.3–78.0, but even these values were higher than the theoretic value 65.7, which is based on the presence of one double bond in the molecule of cholesterol. The Hanus method gave still higher results, 71.4–81.1, while the highest values of all were obtained by the Wijs method, 55.1–158.9, with a tendency to lie above 100. There was a marked tendency, especially in the Hanus and Wijs methods, for the iodine number to become higher, the greater the excess of the iodine reagent. However, the iodine numbers were not simple multiples of 65.7, hence the presence of a second double bond in cholesterol is doubtful.

The gravimetric determination of cholesterol as the free alcohol by modifications of Ritter's method is unsatisfactory. When carbon dioxide was used to neutralize the excess of sodium ethylate, divergent duplicates were obtained, 99.90 and 92.43 per cent. of the cholesterol taken being recovered. When hydrochloric acid was used to neutralize the excess of sodium ethylate, the results were still less satisfactory, 64.34–89.10 per cent. of the cholesterol taken being recovered.

The gravimetric determination of cholesterol as the free alcohol by Cappenberg's method gave excellent duplicates; 94.47 and 94.37 per cent. of the cholesterol taken was recovered.

The gravimetric determination of cholesterol as cholesteryl

benzoate is not quantitative, but 24.29 to 61.79—average 42.86 per cent. of the cholesterol taken—was recovered.

The gravimetric determination of cholesterol as digitonin cholesteride was the most accurate and most satisfactory of the methods studied. From 93.63 to 103.02—average 97.37 per cent. of the cholesterol taken—was recovered.

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Westphalian Coke Oven By-products. ANON. (*Engineer*, May 23, 1913.)—The coke produced in the Ruhr district, Rhenish Westphalia, in 1911, equalled the combined total output of British collieries and gas-works in the same year, and when the British figures for 1912 are available it will be found that the Westphalian pits alone have already surpassed them by many tons. As a result of the increased output of coke from the by-product ovens in the Ruhr, the production of gas and by-products has also expanded. The production of ammonium sulphate, which amounted to only 53,000 tons in Westphalia in 1903, had risen to 236,000 tons in 1911. During the same period the output of coal tar increased from 132,000 tons to 569,000 tons, while that of benzoline developed from 40,000 tons to 70,000 tons in 1911 and 84,000 tons in 1912, and will be further developed by the installation of new plants. The production of illuminating gas from the coke ovens advanced from 393,000 cubic metres in 1903 to 84,594,000 cubic metres in 1911, the gas being largely supplied to towns. Similarly, the output of electrical energy at the Ruhr pits has increased from 58,000,000 kilowatt-hours in 1906 to 592,000,000 kilowatt-hours in 1911, and further extensions were made in 1912. Most of the electrical energy is utilized for the collieries and the auxiliary plant, though the quantity sold to outside parties is continually increasing.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

THE LATENT HEAT OF FUSION OF ICE.

By H. C. Dickinson, D. R. Harper 3d, and N. S. Osborne,
Bureau of Standards.

A DETERMINATION of this constant has been made recently at the Bureau of Standards. The paper † contains a brief summary of the more important contributions on the subject, particularly of those of more recent date. The experimental work which is described at length was carried out in a water calorimeter which permitted a precision to a few parts in ten thousand in calorimetric observations.

Of two methods employed, one is the well-known method of mixtures in which an ice sample of from 100 to 200 grammes weight was allowed to melt in the calorimeter, cooling the water. The other was an electrical method of somewhat higher precision. An ice sample some 500 grammes in weight was put directly into the water and the approximate amount of energy required to melt the ice supplied electrically and measured, the small excess or deficiency being determined from the small rise or fall of temperature of the calorimeter. The usual calorimetric cooling correction was thus rendered relatively very small and the heat capacity of the calorimeter needed to be known only approximately. The ice specimens used were from commercial plate, can, and natural ice, and from ice frozen in the laboratory from double distilled water, both free from air and containing air. They were cut in the form of hollow cylinders to secure a more uniform rate of melting. The samples were kept at the uniform temperature of either— 0.72° or 3.78°—for several hours previous to the experiments, and were so weighed and handled as to introduce each into the calorimeter at the selected constant temperature with no significant error.

Altogether, the heat of fusion of each of 92 samples of pure

* Communicated by the Bureau.

† Reprint 209, Bulletin of the Bureau of Standards.

ice was determined by one of the two methods. The results of the first half of these observations, made before the best experimental conditions were secured, indicate no differences between the heats of fusion of the different kinds of ice greater than the limits of precision,—that is, about one part in a thousand. The latter half show no difference as great as one part in five thousand between the commercial kinds of ice.

The final figure for the heat of fusion of pure ice is 79.63 cal_{15} per gramme mass.

OBSERVATIONS ON OCEAN TEMPERATURES IN THE VICINITY OF ICEBERGS AND IN OTHER PARTS OF THE OCEAN.*

By C. W. Waidner, H. C. Dickinson and J. J. Crowe.

THROUGH the courtesy of the Navy Department the authors were enabled to make a series of observations on board the U. S. S. *Birmingham* and the U. S. S. *Chester* between June 2 and July 10, 1912, to test the utility of accurate measurements of sea-water temperatures in detecting the proximity of icebergs.

A sensitive resistance thermometer built in the form of a plate and mounted against the inside of the ships' three eight-inch plates about six feet below the water line was connected to a Leeds & Northrup recorder. This arrangement gave a continuous record of sea-water temperatures, which would indicate variations of 0.01° or 0.02°, and proved so satisfactory that none of the several other thermometric devices carried on the trip was made use of, with the exception of deep-sea thermometers used for measuring temperatures at considerable depths.

Practically continuous temperature records were obtained for a period of about thirty days, including a score of instances where the ship was within a few hundred yards of icebergs, together with the records on approaching and leaving these bergs. In the majority of these instances the temperature fell slightly upon approaching and rose slightly upon leaving the berg, but this was by no means always true. The variations near icebergs were in general not distinguishable from those observed in other parts of the ocean. It is therefore concluded that at least in the part of

* Reprint 210, Bulletin of the Bureau of Standards.

the North Atlantic where these observations were made, viz., near the northern route of the New York-to-Liverpool steamers, not even the most accurate measurements of sea-water temperature can be relied upon to give warning of the presence of dangerous icebergs.

Other methods of detecting the presence of ice were also tried, such as the density or salinity of the surface water, echoes, both submarine and at night powerful searchlights.

The density of the water does not seem to depend especially upon the presence of icebergs, and neither aërial echoes nor searchlights could be depended upon to give warning of the proximity of icebergs under varying weather conditions. A few experiments upon submarine echoes gave some slight promise of reliable warnings at distances of a mile or two, but the experiments could not be pursued further because of the lack of apparatus.

The conclusions as to the value of temperature records are not in agreement with those of Prof. H. T. Barnes, of Toronto, whose observations made in regions further north indicate a rather definite small rise of temperature of the sea on approaching icebergs.

The use of recording thermometers on shipboard, while perhaps not of great value in locating icebergs, may prove valuable in locating ocean currents and in indicating by a fall of temperature the approach to land or to shallow water.

Electric Railway in Navarre, Spain. Anon. (*Elektrotechn. Zeitschr.*, xxxiv, 27.)—This line runs from Pamplona to Sanguesa, in the Pyrenees district in the north of Spain; the total length is 56 kilometres. It has gradients up to 5 per cent., and is intended for carrying lumber and other kinds of merchandise. It is worked on the single-phase system at 6600 volts and 25 cycles, the pressure being converted by transformers, carried on the trains, to 600 volts. The cars in some cases have four, and in other cases two, motors of 60 horsepower of the Latour type; compressed-air brakes are used to supplement the hand brakes. Portions of the line are worked with an overhead pressure of 600 volts, and special precautions are adopted to prevent the possibility of any accident to the machinery at the points of transition. This is the first single-phase line constructed in Spain, and it has been working successfully for two years.

Influence of the Cooling Medium on the Temperature-rise of Stationary Induction Apparatus. J. J. FRANK and W. O. DWYER. (*Amer. Inst. Elect. Engin. Proc.*, xxxii, 337.)—For some time it has been admitted that the corrections to be applied to the temperature-rise of stationary induction apparatus, when operating under conditions differing from standard, require some little revision. In the first part of the paper the theoretical considerations governing the dissipation of heat from this class of apparatus are given briefly; and the influence of temperature, barometric pressure, and humidity on the emissive constants is briefly discussed. The presence of moisture was expected to have considerable influence on the temperature-rise, but a theoretical analysis shows for ordinary room temperatures the effect can be small, even though the atmosphere be saturated. Exception is made in the case of fog-laden air.

The second part of the paper presents the results of some tests made to check these conclusions. Some tests were made under artificial and some under natural conditions. Recommendations for corrections to be applied and precautions to be taken are given. When possible, apparatus should be tested under conditions similar to those under which it is to operate. When these conditions cannot be maintained the following corrections should be applied: (1) *Variations in Room Temperature.*—On all classes of apparatus, except air-blast, no correction be applied. On air-blast the present recommendations of the A. I. E. E. be followed. On water-cooled apparatus the reference should be the ingoing water, and the temperature of this and of the room should be as near 25° C. as possible. (2) *Variations in Barometric Pressure.*—For self-cooled apparatus the present A. I. E. E. recommendations be followed. For water-cooled apparatus no corrections be applied. For air-blast apparatus double the present A. I. E. E. recommendations be followed. (3) *Variations in Humidity.*—No corrections be applied for variations in humidity except in case of fog-laden air.

Fireproof Porcelain. HEINECKE. (*Chem. Zeit.*, xxxvii, 768.)—The so-called "fireproof" porcelain cooking vessels upon the market can only be regarded as fire-resistant, since in technology the term "fireproof" is restricted to products melting above Seger cone 26. The basis of European hard porcelain is a mixture of 50 parts of clay, 25 of felspar, and 25 of quartz. A body prepared from a mixture of 30 parts Zettlitz kaolin, 52 of felspar, and 45 of alumina, burned at Seger cone 18, or preferably fused in an electric furnace, does not melt below Seger cone 35 or 36, but, since it softens without melting at high temperatures, it is advisable to replace the felspar by an intimate mixture of 1 mol. of felspar with 3 to 6 mols. of alumina. Very compact and fire-resistant masses, melting at Seger cone 37, may be prepared from a well-burned mixture of alumina and magnesia.

THE FRANKLIN INSTITUTE

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, September 3, 1913.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, September 3, 1913.

MR. J. A. P. CRISFIELD *in the Chair.*

Amendments to the 1909 Regulations as proposed by a special sub-committee were considered and adopted in their final form.

The following reports were presented for first reading:
No. 2522.—Gaede's Molecular Air-Pump.
No. 2527.—Norton Alundum.
The following new subjects were recommended for examination:
No. 2584.—The Humphrey Pump.
No. 2585.—Ridgway's Steam Hydraulic Elevator.
The following application for investigation was accepted:
No. 2586.—Dobbin's Daylight Rods.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

Elections to Membership.

(Stated Meeting of the Board of Managers, August 13, 1913.)

RESIDENT.

MR. CHAS. W. MESSNER, 3704 North Broad Street, Philadelphia, Pa.
MR. OTTO MOESSNER, Machen & Mayer Electrical Manufacturing Company, Twenty-first Street and Fairmount Avenue, Philadelphia, Pa.
DR. JOSEPH P. REMINGTON, Dean, Philadelphia College of Pharmacy, 145 North Tenth Street, Philadelphia, Pa.
MR. UTLEY WEDGE, Ardmore, Pa.

NON-RESIDENT.

PROF. ERNEST A. HERSAM, University of California, Berkeley, Cal.
MR. MARTIN HILL ITTNER, Colgate & Co., Jersey City, N. J.

(Stated Meeting of the Board of Managers, September 10, 1913.)

RESIDENT.

MR. CHAS. HAY SPAYD, C. E. Johnson & Co., 509 South Tenth Street, Philadelphia, Pa.

MR. SIMEON TRENNER, 6328 Jefferson Street, Germantown, Philadelphia, Pa.

MR. D. ROBERT YARNELL, 316 Preston Street, Philadelphia, Pa.

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MR. CECIL F. BACKUS, Atlas Powder Company, Wilmington, Del.

MR. A. W. K. BILLINGS, Apartado 491, Barcelona, Spain.

MR. GEORGE B. CHORPENING, Box 197, Clarksburg, W. Va.

MR. H. B. SARGENT, Sargent & Co., New Haven, Conn.

MR. ELMER A. SPERRY, The Sperry Gyroscope Company, Manhattan Bridge Plaza and Flatbush Avenue, New York, N. Y.

Changes of Address.

PROF. F. W. BUSHONG, Mellon Institute of Industrial Research, Pittsburgh, Pa.

MR. BURDETTE DALE, 1127 Douglas Avenue, Ames, Iowa.

MR. LEON B. EICHENGREEN, Counties Gas and Electric Company, Ardmore, Pa.

DR. ERNST FAHRIG, 207 Metropolitan Avenue, Atlantic City, N. J.

LIEUT. R. E. GILLMOR, 57 Victoria Street, London, England.

MR. FRED. T. HASCHKA, 129 West Sixty-ninth Street, New York City, N. Y.

MR. EDWARD V. MCCAFFREY, McCaffrey File Company, Philadelphia, Pa.

MR. F. R. PLEASONTON, International Motor Company, Plainfield, N. J.

DR. ISHAM RANDOLPH, 1807 Commercial National Bank Building, Adams and Clark Streets, Chicago, Ill.

MR. L. D. RICKETTS, Warren, Ariz.

DR. L. M. TOLMAN, 1408 Emerson Street, Washington, D. C.

MR. ORVILLE WRIGHT, 1127 West Third Street, Dayton, Ohio.

LIBRARY NOTES.

Gifts.

American Society of Mechanical Engineers Transactions, vol. 34, 1912. New York, 1913. (From the Society.)

Baldwin Locomotive Works, Record of Recent Construction, Nos. 1–40, 55 and 56. Philadelphia. (From the Works.)

British Columbia Minister of Mines, Annual Report, 1912. Victoria, 1913. (From the Minister.)

Buffalo, Rochester & Pittsburgh Railway Company, 28th Annual Report, 1913. New York, 1913. (From the Company.)

Canada Department of Mines: The Nickel Industry, by A. P. Coleman, and Sections of the Sydney Coal Fields, Cape Breton, by Joseph G. S. Hudson. Ottawa, 1913. (From the Department.)

Canadian Pacific Railway Company, Annual Report, June 30, 1913. Montreal, 1913. (From the Company.)

Chicago Department of Public Works, 37th Report, 1912. Chicago, 1913. (From the Department.)

D'Este Steam Engineers' Manual, 2nd edition, 1913. Boston, 1913. (From Julian D'Este Company.)

Finland Patent Office: Yrkesinspektörerans i Finland Arsberättelser, 1911. Suomen Ammattientarkastajain Toimintakertomukset, 1911. Teollisnustilastoa 28, 1911. Industristatistik 28, 1911. Helsingfors, 1913. (From the Patent Office.)

Illinois Railroad and Warehouse Commission, 42nd Annual Report, 1912, vols. 1 and 2.

Institution of Civil Engineers, Minutes of Proceedings, vol. 192, 1912–13. London, 1913. (From the Institution.)

Instituto y Observatorio de Marina de San Fernando, Anales seccion 2ª, 1912. San Fernando, 1913 (From the Institute.)

Iron and Steel Institute Journal, vol. 87, 1913. London, 1913. (From the Institute.)

John Crerar Library, A List of Current Medical Periodicals, ed. 2, April, 1913. Chicago, 1913. (From the Library.)

Los Angeles Public Library, 25th Annual Report, 1912–1913. Los Angeles, 1913. (From the Library.)

Lynn Commissioner of Water and Water Works, Annual Report, 1912. Lynn, Mass., 1913. (From the Commissioner.)

Maryland Institute for the Promotion of the Mechanic Arts, Announcement School of Art and Design, 1913–1914. Baltimore, 1913. (From the Institute.)

Newark Free Public Library, 24th Annual Report, 1912. Newark, N. J., 1913. (From the Library.)

New South Wales, Department of Mines: Mineral Resources, No. 17, Report on the Cobar Copper and Gold-Field, by E. C. Andrews. Sydney, 1913. (From the Department.)

New York State Educational Department, Annual Report, 1913, and Proceedings of the Dedication New York State Education Building, October, 1912. Albany, 1913. (From the New York State Library.)

New Zealand Institute, Transactions and Proceedings, vol. 45, 1913. Wellington, 1913. (From the Institute.)

Ohio Geological Survey, Bulletin 4th series, No. 17, Conemaugh Formation in Ohio, by D. Dale Condit. Columbus, 1912. (From the Survey.)

Ontario Agricultural Societies, 13th Annual Report, 1913. Toronto, Can., 1913. (From the Ontario Department of Agriculture.)

Oregon Railroad Commission, Sixth Annual Report, 1912. Salem, 1913. (From the Commission.)

Pennsylvania Academy of the Fine Arts, School Circular, 1913–1914. Philadelphia, 1913. (From the Academy.)

Pennsylvania Chestnut Tree Blight Commission, Report July 1 to December 31, 1912. Harrisburg, 1913. (From the Commission.)

Philadelphia Maritime Exchange, 38th Annual Report, 1913. Philadelphia, 1913. (From the Exchange.)

Rainfall of the Bombay Presidency, vol. 2, 1912. Bombay, 1912. From the Meteorological Department of India.)

Sayings and Writings About the Railways by Those Who Have Managed Them and Those Who Studied Their Problems. New York, 1913. (From the Bureau of Railway Economics, Washington, D. C.)

Texas Academy of Science, Transactions, vol. 12. Austin, 1913. (From the Academy.)

United States National Museum, Annual Report, June 30, 1912. Washington, D. C., 1913. (From the Smithsonian Institution.)

U. S. War Department, Tests of Metals, 1912. Index to Tests of Metals, 1881–1912. Washington, 1913. (From the Department.)

University of Buffalo, Medical Department, Sixty-eighth Announcement, 1913–1914. Buffalo, 1913. (From the University.)

University of Idaho, Catalog 1912–1913. Moscow, 1913. (From the University.)

University of Nevada, Register 1912–1913. Reno, 1913. (From the University.

Western Australia Department of Mines, Report 1912. Perth, 1913. (From the Department.)

Wisconsin Railroad Commission, Reports vols. 1–8, July 20, 1905, to March 12, 1912. Madison, 1908–1912. (From the Commission.)

BOOK NOTICES.

GENERAL AND INDUSTRIAL CHEMISTRY, by E. Molinari. Vol. II, Organic. Published by P. Blakiston's Son & Co. 770 pages (24.5 × 15 cm.). Price, $6.

This is the companion volume to the "Inorganic Chemistry" of the same author, the translation of which appeared some time ago. The immediate success of both books shows that the author's plan of treating general chemistry, along with technology, in the same volume has met with wide approval. In spite of this fact, the advantages of the combination are far from obvious to the reviewer. Perhaps the point may be that the technology keeps the interest of the student alive and acts, so to speak, as a sugar-coating for the purely scientific portion.

Although the reviewer is doubtful with respect to the wisdom of the plan, he is able to give unqualified commendation to the manner in which it has been carried out. The book is much longer than its eight hundred pages would indicate, for the pages are large and the typography very close. It offers a vast amount of information, which is surprisingly accurate and modern. The translator, Dr. Pope, has done his work very well indeed.

The prices of chemicals which are of technical importance are given, often in pounds, shillings, and pence. In view of the rapid variations to which prices are subject, the value of these data is rather open to question.

In the discussion of the theory of valence on page 15 the spelling "Cooper" instead of Couper is undoubtedly a misprint. The publishers have fallen into a little unwise economy on page 70, where Fig. 90, with its Italian words in the diagram, presents a singular appearance. It would have cost very little to have a new cut made and would have avoided a blemish.

To those who think it wise to amalgamate scientific chemistry with technology, this book can be heartily recommended. Professor Molinari's "Inorganic Chemistry" on the same plan has achieved a substantial success, and the present volume is superior to its predecessor.

ROBERT H. BRADBURY.

PENNSYLVANIA CHESTNUT TREE BLIGHT COMMISSION. Report July 1 to December 31, 1912. 67 pages, illustrations, maps, plates, 8vo. Harrisburg, State Printer, 1913.

This report gives an interesting summary of the work done in the effort to combat and eradicate the destructive chestnut tree blight.

The introduction refers to the possibility of a serious timber famine confronting the American people, and the absolute necessity for concerted action of the friends of forestry and forest conservation to avert a threatened crisis. Attention is called to the fact that it costs fully one-third more to-day to buy hemlock and other common varieties of building lumber than the same material would have cost only five years ago.

The chestnut blight occasioned a loss of many millions of dollars to the timber owners of Pennsylvania, and since the Commission decided to discontinue its operations especial interest has been aroused, as the total extermination of our native chestnut is threatened. At least a dozen other States continue the warfare against the disease. The Bureau of Plant Industry of the U. S. Department of Agriculture is coöperating in a practical manner through a large pathological force.

The reports of the several executive officers and others indicate very clearly that much progress has been made in the study of the proper treatment of infected chestnut trees. Especial attention was devoted to the utilization feature, and in this manner the owner of blighted timber was able to secure a ready market for its disposal at fair prices. The educational work enabled owners of trees to recognize the disease, and to obtain needful information of much value without cost as to the treatment of diseased trees.

The blight has been eradicated from the western part of the State, but spot infections will most likely reappear. Unless timber owners watch carefully, and destroy such infections promptly, the blight will spread rapidly and further heavy losses will follow. In Eastern and Southern Pennsylvania a large percentage of the chestnut was badly infected before the Commission was created.

Recent information shows that the chestnut blight is prevalent in China, and, therefore, probably of foreign origin. Hence there is greater hope now that continued scientific research work such as is in progress in this country

will reveal the much-needed remedial measures to prevent the threatened total extermination of our native chestnut trees.

THE SYMPTOMS OF THE CHESTNUT TREE BLIGHT AND A BRIEF DESCRIPTION OF THE BLIGHT FUNGUS, by F. D. Heald, Pathologist. 15 pages, 16 plates, 8vo. Harrisburg, Pennsylvania Chestnut Tree Blight Commission, 1913.

Bulletin No. 5 of the Commission has just come from the press and gives a complete description of the chestnut tree blight.

The disease is a parasitic fungous growth that girdles trunks, branches, and twigs of the chestnut trees, whether large or small, and kills them.

An object lesson of special importance consists in the remarkable fact that to-day there does not exist a single live chestnut tree in Greater New York, where the species thrived in great abundance only a few years ago. In Forest Park, New York, a well-known and attractive resort, there were included amongst its wealth of trees over 17,000 chestnut trees, many being of great age and rare beauty. To-day not a single chestnut tree remains in that park, all having been destroyed by the blight.

PUBLICATIONS RECEIVED.

U. S. War Department: Annual reports 1912 (in four volumes). Volume I, Reports of the Secretary of War, the Chief of Staff, the Adjutant-General, the Inspector-General, the Judge Advocate-General, the Quartermaster-General, the Commissary-General, the Surgeon-General, the Paymaster-General, the Chief of Ordnance, the Chief Signal Officer, the Chief of Coast Artillery. Volume II, Reports of the Chief of Engineers (without appendices). Volume III, Reports of Eastern, Central, Western, Philippines Division, Military Academy, Military Arts. Volume IV, Reports of the Chief, Bureau of Insular Affairs, Philippine Commission, Governor of Port Rico. 4 volumes, illustrations, plates, maps, 8vo. Washington, Government Printing Office, 1913.

Pennsylvania Chestnut Tree Blight Commission: Report July 1 to December 31, 1912. 67 pages, illustrations, maps, 8vo. Bulletin No. 5. The Symptoms of Chestnut Tree Blight and a Brief Description of the Blight Fungus, by F. D. Heald, Pathologist. 15 pages, 16 plates, 8vo. Harrisburg, State Printer, 1913.

Michigan College of Mines: Year Book, 1912–1913. Announcement of Courses, 1913–1914. 130 pages, maps, 12mo. Houghton, College, 1913.

Mellon Institute of Industrial Research and School of Specific Industries: Smoke Investigation Bulletin No. 2, Bibliography of Smoke and Smoke Prevention, compiled by Ellwood H. McClelland, Technology Librarian, Carnegie Library of Pittsburgh. 164 pages, 8vo. Pittsburgh, Pa., University of Pittsburgh, 1913.

Canada Department of Mines, Mines Branch: The Nickel Industry:

with Special Reference to the Sudbury Region, Ontario, by A. P. Coleman, Ph.D. 206 pages, illustrations, plates, maps, 8vo. Ottawa, Government Printing Bureau, 1913.

U. S. Census Bureau, Department of Commerce: Forest Products No. 2, Lumber, Lath and Shingles, 1911. Forest Products No. 8, Crossties Purchased, 1911. Forest Products No. 9, Poles Purchased, 1911. 3 pamphlets, 8vo. Washington, Government Printing Office, 1913.

U. S. Office of Public Roads, Department of Agriculture: Circular No. 100, Typical Specifications for the Fabrication and Erection of Steel Highway Bridges. 25 pages, 8vo. Washington, Government Printing Office, 1913.

U. S. Bureau of Mines, Department of the Interior: Bulletin 53, Mining and Treatment of Feldspar and Kaolin in the Southern Appalachian Region, by A. S. Watts. 170 pages, illustrations, plates, maps, 8vo. Bulletin 59, Investigations of Detonators and Electric Detonators, by Clarence Hall and Spencer P. Howell. 73 pages, illustrations, plates, 8vo. Bulletin 56, First Series of Coal-dust Explosion Tests in the Experimental Mine, by George S. Rice, L. M. Jones, J. K. Clement, and W. L. Egy. 115 pages, illustrations, plates, 8vo. Technical Paper 15, An Electrolytic Method of Preventing Corrosion of Iron and Steel, by J. K. Clement and L. V. Walker. 15 pages, illustrations, 8vo. Technical Paper 47, Portable Electric Mine Lamps, by H. H. Clark. 13 pages, 8vo. Monthly Statement of Coal-mine Fatalities in the United States, May and June, 1913, compiled by Albert H. Fay. 2 pamphlets, 8vo. Washington, Government Printing Office, 1913.

U. S. Coast and Geodetic Survey, Department of Commerce: Results of Observations Made at the United States Coast and Geodetic Survey Magnetic Observatory at Cheltenham, Maryland, 1911 and 1912, by Daniel L. Hazard, Computer, Division of Terrestrial Magnetism. 98 pages, plates, quarto. Washington, Government Printing Office, 1913.

Harrison Safety Boiler Works: Catalogue No. 550, Section A: Live Steam Separators; B: Live Steam Separators and Receivers; C: Oil Separators; D: Vacuum Oil Separators. 4 pamphlets, illustrations, 8vo. Philadelphia, Works, 1913.

An Amendment to the Constitution: Prohibiting the Sale, Manufacture, and Importation of Distilled Liquor, speech of Hon. John D. Works, of California, in the Senate of the United States, June 21, 1913. 8 pages, 8vo. Washington, Government Printing Office, 1913.

Werden die Zeichen der Wechselstromtelegraphie verlängert (mit Erwiderung von Herrn Dr. K. W. Wagner). 2 pages, illustrations, quarto. Reprinted from the *Elektrotechnische Zeitschrift*, Heft 21. Berlin, Julius Springer, 1913.

Canada Department of Mines, Mines Branch: Sections of the Sydney Coal Fields, Cape Breton, by Joseph G. S. Hudson. Special Edition. International Geological Congress, Twelfth Session, 1913. 6 pages, plates, maps, 8vo. Ottawa, Government Printing Bureau, 1913.

Royal Institution of Great Britain, Weekly Evening Meeting: January 17, 1913.—Some Further Applications of the Method of Positive Rays,

Prof. Sir. J. J. Thomson. February 13, 1913.—Gyrostats and Gyrostatic Action, Prof. Andrew Gray. March 14, 1913.—Great Advance in Crystallography, A. E. H. Tutton. April 4, 1913.—The Spectroscope and Organic Chemistry, James J. Dobbie, Esq., M.A., LL.D. April 11, 1913.—The Winds in the Free Air, Charles J. P. Cave, Esq., M.A. April 18, 1913.—Applications of Polarized Light, Thomas Martin Lowry, Esq., D.Sc. 6 pamphlets, illustrations, 8vo. London, Institution, 1913.

An Active Modification of Nitrogen. R. J. STRUTT. (*Roy. Soc. Proc.*, A 88, 539).—This active modification of nitrogen is produced by the electric discharge. For preparing and storing the nitrogen to be submitted to the electric discharge two 15-litre aspirator bottles are arranged as a gas-holder in the usual way, a muslin bag containing chopped phosphorus being suspended in the gas space. The gas-holder is filled with commercial nitrogen. All traces of oxygen are removed in two to three hours, and, when the fumes arising from the phosphorus have subsided, the gas is ready for use. On its way to the discharge tube the nitrogen is dried by passing it first through a column of phosphorus pentoxide, 30 cm. by 5 cm., and then through a tube packed with copper gauze and cooled with liquid air. As the gas is withdrawn from the holder the water rises and finally drowns the phosphorus, dissolving out the oxides and leaving it ready for further use. The gas-holder should be covered with a black cloth to protect the phosphorus from the action of light. Contrary to statements by other workers, the phenomena of active nitrogen are not due to the presence of traces of oxygen. Oxygen, in fact, acts unfavorably, and 2 per cent. prevents the phenomena altogether. Hydrogen and carbon dioxide are less harmful than oxygen, but even traces of water vapor are very prejudicial. Active nitrogen combines with the vapor of mercury, cadmium, zinc, arsenic, sodium, and sulphur to form nitrides which are decomposed by water or potassium hydroxide solution with the evolution of ammonia. Carbon bisulphide yields polymeric carbon monosulphide and a blue polymeric nitrogen sulphide. Sulphur chloride gives ordinary yellow nitrogen sulphide.

The Influence of "Drawing" on Metallurgical Products. L. GUILLET. (*Rev. Mét.*, x, 769.)—Drawing raises the elastic limit, increases the brittleness, and reduces the elongation of metals. Experiments made to ascertain the difference in behavior of annealed and rolled plates of pure aluminum, and of aluminum alloys, in water, and solutions of sodium hydroxide (1 per cent.), sodium chloride (1, 5, and 10 per cent.), hydrochloric acid (1 per cent.), and magnesium chloride (1 per cent.), showed that while in general the rolled plates were attacked to a greater extent than the annealed plates, this result was not invariable.

"VOLCANIC DUST AND OTHER FACTORS IN THE PRODUCTION OF CLIMATIC CHANGES AND THEIR POSSIBLE RELATION TO ICE AGES."

A CORRECTION.

The Editor, JOURNAL OF THE FRANKLIN INSTITUTE:

DEAR SIR:

Allow me to ask that you kindly note the following errata in my recent article on volcanic dust:

Page	for	write
137, line 4 from top	"brothers"	cousins
138, line 10 from top	"	"
140, line 12 from top	"	"
142, equation 1	"$\left(1 + \frac{B}{rp}\right)$"	$\left(1 + \frac{B}{rp}\right)$
142, middle of page	"$\left(1 + A\frac{l}{r}\right)$"	$\left(1 + A\frac{l}{r}\right)$
148, line 19 from bottom	"otherwise"	other kind
162, line 4 from bottom	"spot minima"	spot maxima
168, second equation from top	"34×10^4"	$34 \pi 10^4$

In regard to the viscosity of dry air, it has just been shown by Millikan (*Ann. der Phys.*, 9, p. 759, 1913) that at the absolute temperature T

$$M_T = \frac{150.387^{\frac{3}{2}}}{T + 124} \times 10^{-7}$$

According to this equation, page 143 should be corrected as follows:

$$M_{-55} = 1416 \times 10^{-7}$$

Velocity and time of fall.

Height in kilometres	Barometric pressure	Centimetres per second	Seconds per centimetre
40	1.84	1.0214	0.979
30	8.63	0.2414	4.143
20	40.99	0.0745	13.427
15	89.66	0.0503	19.874
11	168.00	0.0408	24.492
0	760.00	0.0259	38.603

While all the foregoing corrections are desirable, they do not affect the argument nor alter in the least any of the conclusions.

Yours truly,

W. J. HUMPHREYS.

CURRENT TOPICS

Uranium and Radium. C. L. PARSONS. (*Min. and Eng. World*, May 10, 1913.)—All the radium placed on the market in the last few years has been produced in Europe, yet a large portion of this output has come from American ores. At least 20 to 25 tons of high-grade pitchblende have been exported. During the last year carnotite containing 28.8 tons of pitchblende, from which 11.43 grammes of radium bromide could be obtained, were produced. All this ore was shipped abroad for the extraction of radium. The value of the radium salts extracted would be about $530,000. The total supply of radium salts from all other sources was 3.65 grammes of radium chloride, basing the production of the Austrian mines for 1912 upon that of 1911, which is known. Small quantities of pitchblende have been found in Connecticut, and in the feldspar quarries of North Carolina. Practically all the American output has come from the mines in Quartz Hill, Gilpin County, Colorado. Carnotite consists chiefly of potassium uranyl vanadate, but also contains small amounts of barium and calcium compounds. Necessarily it also contains radium, although it has not yet been definitely established that the uranium and radium are in equilibrium as they are in pitchblende. In carnotite the amount of radium is not far from the equilibrium ratio, and in the calculations given above an allowance of 10 per cent. has been made to cover this possible deficiency. The more important deposits are scattered over Colorado and Utah. Carnotite always carries vanadium as well as uranium and radium, but is purchased almost wholly on its radium content, comparatively little being allowed for its vanadium. Ore with 2 per cent. uranium oxide is now worth approximately $75 per ton f. o. b. New York. In mining these carnotite ores probably 5 tons of material capable of concentration are wasted for every ton sent to market. One of the problems before the Bureau of Mines is to develop methods for concentrating these ores.

Cellulose from Pea and Bean Stalks. O. REINKE. (*Chem. Zeit.*, xxxvii, 601.)—On digestion with not more than 6 to 7 per cent. of caustic soda, waste pea and bean stalks readily yield cellulose in larger proportion and better quality than that obtained from asparagus stalks. The cellulose is easily bleached by bleaching powder liquor, and still better by a 1 per cent. solution of potassium permanganate, followed by sulphurous acid. The celluloses are free from knots and consist of small fibres, fine, woolly, and brilliant white. The cellulose is very suitable for the manufacture of nitrocellulose, viscose, etc.

Electrical Emissivity of and Disintegration of Hot Metals. J. A. HARKER and G. W. C. KAYE. (*Roy. Soc. Proc.*, A 88, 522.)—The metals were heated by alternating current, mostly in nitrogen at reduced pressure. Positive electricity was emitted at temperatures from about 1000° C. to 1400° C.; and for metals which melt within this range a sudden and marked increase in the positive current often occurred at the melting-point, probably owing to the sudden release of occluded gas. The positive current appears to be increased in presence of oxygen. Negative electricity predominates at higher temperatures, and increases rapidly with the temperature. With carbon in air at atmospheric pressure, a negative ionization current of 3½ ampères was obtained. At moderate pressures the negative currents appear to be largely increased when considerable sputtering of the metal occurs; they are probably due to a chemical reaction between the metal and the surrounding gas. It is considered that the deposits obtained in these experiments are due not only to volatilization and condensation, as ordinarily understood, but also to straight-line emission of particles (compare Reboul and De Bollemont). Carbon becomes soft and plastic, and readily sublimes, at about 2500° C. A metal tube cooled by water was surrounded by a carbon tube, and the latter was heated by low-voltage alternating current to about 2500° C., hydrogen being passed between the two tubes. After about 30 minutes, the metal tube was coated with a deposit of carbon sufficiently hard and coherent to be removed in short lengths. It is suggested that carbon of high purity could be obtained in this way by fractional distillation.

Colorado Coal Production. (*U. S. Geological Survey.*)—Coal mining as an industry in Colorado began in 1864, when a production of 500 short tons was recorded. In 1876 the production reached for the first time a total exceeding 100,000 tons, and six years later, in 1882, it had reached the million-ton mark. Since that date the increase has been almost uninterrupted. The production exceeded 3,000,000 tons in 1890; 10 years later it had grown to over 5,000,000 tons, and in 1910 it exceeded 11,000,000 tons, but in 1912 it fell just below the 11,000,000-ton mark.

Cistern Filters Do Not Remove Germs. (*U. S. Geological Survey.*)—Cisterns that are properly constructed and receive rain water from roofs generally afford water of good sanitary quality, but if water of doubtful quality is stored in cisterns the supply is, of course, not safe for domestic use. Filters used in connection with cisterns are of value in making the water clear, but are generally of no value in removing disease germs. Many cisterns are divided into two parts by a brick wall, the water being admitted into one compartment and drawn from the other. In such cisterns the water passes through the brick and in that way is improved in clearness and color, but not generally in sanitary quality.

Extraction of Thoria from Monazite Sand. F. WIRTH. (*Chem. Zeit.*, xxxvii, 773.)—The formation of sparingly soluble double sulphates of earth metals is avoided by generating the anion of hypophosphoric acid directly in the acid liquor resulting from the decomposition of monazite sand. This is done by the anodic oxidation of copper phosphide in the solution, after first neutralizing the free acid present, so far as to leave the phosphates just dissolved. With an electromotive force of about 10 volts the hypophosphate ions are at once converted into the insoluble thorium salt. Oxidizers, such as hydrogen peroxide, which give ozone on electrolysis, facilitate the process. Thorium may also be precipitated by alkali hypophosphate from feebly alkaline solution (*e.g.*, of the tartrate), and the solubility of thorium hypophosphate in a large excess of ammonium oxalate may be utilized for separating thorium, in alkaline solution, from trivalent earths, which are insoluble in ammonium oxalate. The thorium hypophosphate is treated as previously described. Cerium may be detected in neutral solution by adding 5 c.c. of 10 per cent. ammonium tartrate solution and 5 c.c. of dilute ammonia; the solution becomes yellow or yellowish-brown on boiling, or in the cold with 0.1 to 0.5 per cent. of cerium. Hydrogen peroxide gives a brown precipitate of cerium peroxide with concentrated alkaline solutions of cerium tartrate, and a coloration may be detected with 0.0002 gramme of cerium peroxide in 100 c.c.

The Periodic System and the Radio-Elements. A. S. RUSSELL. (*Chem. News*, cvii, 49.)—It has been recognized that some of the longer-lived radio-elements, such as Ra, RaF, and RaEm, have definite places in the periodic system of the chemical elements. In this paper the whole of the radio-elements are dealt with. The rules given are: (1) Whenever an α-particle is expelled by a radio-element the group in the periodic system to which the resultant product belongs is either two units greater or two units less than that to which the parent body belongs. (2) Whenever a β-particle or no particle is expelled, with or without the accompaniment of a γ-ray, the group in the periodic system to which the resultant product belongs is one unit greater or one unit less than that to which the parent product belongs.

Devitrification of Quartz Glass. A. C. MICHIE. (*Chem. Zeit.*, xxxvii, 589.)—The transformation of quartz glass into cristobalite at high temperatures was noted by Day and Shepherd, and more recently by Rieke and Endell. Thomas stated that small additions of titania or zirconia counteracted this tendency. The author contradicts this statement and affirms that vitreosil, the English fused silica, is less liable to devitrification than siloxide and other glasses which contain zirconia or titania. Seger and Cramer support this view. The method of testing consists of heating the ware at high temperatures in oxidizing and reducing atmospheres.

Coal-Dust Explosions. (4th *Report of Explosions in Mines Committee.*)—While there is no well-defined border line between "inflammation" and "explosive combustion" in the case of gaseous mixtures, a distinction may be drawn in the case of mixtures of coal dust and air. During the "inflammation" of dust from bituminous coals the flame is largely propagated by the burning of gases distilled from the dust, but during "explosive combustion" the portion of each dust particle that aids in propagating the flame is burned as a whole. A coal dust containing 16 per cent. of volatile matter caused an explosion as violent as one caused by a dust containing 35 per cent. of volatile matter, while explosions of equal or greater violence were caused by wood charcoal. Experiments made by R. V. Wheeler in the Altofts gallery are described which confirm this conception of two distinct stages—"inflammation" and "explosive combustion"—in the combustion of mixtures of coal dust and air. The combustion of the mixture was of the nature of an "inflammation" until it had travelled some distance along the gallery, when it was suddenly converted into "explosive combustion," marked by a sudden and considerable rise of pressure. Attention is drawn to the connection between these results and the view advanced by Blackett (*Trans. Fed. Inst. Min. Eng.*, 1894, vii, 54) as to the effect of a "pioneering cloud" in dust explosions. The experiments show that, for a propagating inflammation to take place in a mine, the concussion of a blown-out or overcharged shot, or of a firedamp explosion, is not essential. A flame, without any concussion, can ignite a ready-formed dust cloud, and the inflammation will spread through the cloud with increasing velocity and, if the conditions remain favorable, will ultimately change to "explosive combustion." Constrictions or obstructions cause the transition from inflammation to explosive combustion to take place at a much earlier period than in a smooth gallery, though they do not necessarily increase the ultimate violence of the explosion.

Refractive Index of Selenium. W. S. GRIPENBERG. (*Phys. Zeitschr.*, xiv, 123.)—When melted selenium is pressed between plate glass, sheets from 20 to 250 $\mu\mu$ in thickness may be obtained. Notwithstanding the rapid cooling, small circular portions, less than 0.2 mm. in diameter, become crystalline. They show much greater absorption of light than the amorphous selenium, and have a higher refractive index. The interference colors are of a higher order in the crystalline selenium than in amorphous selenium. They show that the refractive index is from 1.16 to 1.27 times greater. This gives a refractive index 3.5 for sodium light, or the highest refractive index known among elementary substances. This result was confirmed by making a film of selenium on glass by cathode disintegration and crystallizing one-half of it. The crystallized half showed narrower interference rings than the amorphous half, the diameters being as 4 to 5.

Influence of Phosphorus on the Properties of Iron. E. D'AMICO. (*Ferrum*, x, 289.)—Three series of experiments were made on the natural, annealed, and chilled material of 12 samples with increasing phosphorus content, 0.012 to 1.242 per cent. The chemical composition, specific gravity, and metallographical characters are given. The conclusions reached are: The increase in hardness is nearly proportional to the phosphorus content, about 12 Brinell units per 0.1 per cent. increase. Elasticity is increased about 2.7 kilos per square millimetre per 0.1 per cent. Tensile strength increases until 0.5 per cent. phosphorus is reached, beyond which it decreases. Expansion and contraction decrease as the tensile strength increases with low phosphorus contents; but with high phosphorus they are practically *nil*. Above 0.24 per cent. phosphorus the metal is very brittle. The electric conductivity is lowered, but the magnetic properties are influenced only by a high phosphorus content, the latter counteracting the effect of the preliminary treatment of the material. Numerous tables, diagrams, and microphotographs are given.

Rare Metals in Copper. ANON. (*Brass World*, ix, No. 8, 279.)—Some copper ores contain considerable quantities of rare metals, and many copper refiners take the precaution of saving them by the electrolytic refining process. In a paper in the *Transactions of the American Institute of Mining Engineers*, A. Eilers gives the proportions of rare metals obtained from several varieties of copper. The copper from Garfield, Utah, contains in 5000 tons:

Gold	14,400 ounces
Silver	174,000 ounces
Platinum	17 ounces
Palladium	59 ounces
Selenium	2,800 pounds
Tellurium	277 pounds
Bismuth	305 pounds
Nickel	2,000 pounds

Selenium was present in all the varieties of copper examined, and nearly always in greater quantity than the tellurium. Some of the copper contained no tellurium.

Whale Oil Refining. ANON. (*Board of Trade Jr.*, May 29, 1913.)—A Norwegian-German company near Fredrikstad, with a capital of $833,500, has been formed to work a new German method of oil refining. The Hafslund Falls will generate the electric power required, and will also manufacture by electrolysis the hydrogen required to convert the purified whale oil into a solid neutral fat. It is estimated that the factory will consume about 300 barrels of oil daily.

Concentration of Pitchblende. H. E. WOOD. (*Eng. and Min. J.*, xcv, 1164.)—Numerous commercial tests have shown that the usual process of concentrating pitchblende ores to remove silica results in a loss of upwards of 50 per cent. of the pitchblende. In the following process about 90 per cent. of the pitchblende is recovered, and the concentrate will contain from 45 to 56 per cent. uranium oxide. The ore is crushed to 20-mesh size, roasted, the iron oxide separated magnetically, and then the uranium oxide by a wet or dry gravitation process. In the case of carnotite ores the vanadium oxide may be removed by shaking the crushed ore with water and collecting the slime for further concentration. By this means an ore containing from 1 to 2 per cent. of uranium and vanadium oxides will yield a concentrate containing from 75 to 85 per cent. of the oxides. After removing the vanadium and uranium the ore can be used in the preparation of radium.

Pulverized Coal as a Fuel. H. R. BARNHURST. (*Met. and Chem. Eng.*, xi, 127.)—It is stated that coal properly pulverized and burned may be made to yield higher economic results than are attainable by any other means. The proper conditions are: (1) The coal must be dried to not exceeding 1 per cent. of moisture. (2) It must be pulverized to a high degree of fineness. (3) It must be projected into a chamber hot enough to cause instant deflagration. (4) It must be supplied with air sufficient to yield the oxygen necessary to burn the carbon at once to CO_2. These four requirements are discussed in detail, with special attention to (3) and (4), which have hitherto not been sufficiently considered by engineers. Very high temperatures are attainable with pulverized fuel; thus

1 pound carbon with 11.6 pounds air	Normal	4859° F.
1 pound carbon with 13.92 pounds air	20 per cent. excess	4102° F.
1 pound carbon with 16.24 pounds air	40 per cent. excess	3550° F.
1 pound carbon with 18.56 pounds air	60 per cent. excess	3129° F.
1 pound carbon with 20.88 pounds air	80 per cent. excess	2797° F.
1 pound carbon with 23.20 pounds air	100 per cent. excess	2529° F.

In practice the fireman soon learns how to judge whether the fire is hot enough by its color and the length of the flame. The better the conditions, the shorter and whiter the flame will be. The temperature is generally kept down to the limit desired by admitting excess air. With regard to protecting the furnace lining against the destructive effect of these high temperatures, much of the trouble has arisen from the gases impinging on the surface walls at points where the direction of the gas travel changes, and from too high velocity of the gases due to contracted ports. If the greater part of the heat is largely absorbed by the charge, the waste gases will be proportionately less active in scouring the brickwork. In almost any construction, except perhaps a rotary kiln, it is necessary to change the

direction of the gases on their passage to the flue. This change of direction causes the gases to impinge upon the diverting bricks with an energy proportional to their velocity. At these points the brick can be protected by a system of water-cooled pipes embedded in the walls. The brick may frit to some extent until the protected area is reached, when the fritting will be arrested. The surprisingly small quantity of water which it is necessary to introduce to keep the temperature of the outlet below 200° F. proves that the cooling effect is limited to a prevention of cumulative action, and is no perceptible drawback to the efficiency.

Manufacture of Chilled Iron Car-wheels. F. C. WEBER. (*Metal. and Chem. Eng.*, xi, 92.)—It is difficult to make plain, chilled iron car-wheels of uniform quality from the usual mixture of pig-iron, old car-wheels, and steel and malleable iron scrap. Uneven composition is often shown by brown spot flaws between the tread and the flange; and these brown spots may be due to the viscosity of the molten iron at the time of pouring, which prevents it filling the mould solidly. This becomes oxidized to Fe_3O_4, and during service becomes a well-defined crack, which is gradually covered with Fe_2O_3. Chilled iron car-wheels are also subject to defects technically known as "bones." These are of two distinct kinds: they may be a segregation of slags or may consist of a hard spot of steel. The latter case may arise from the steel scrap fed into the cupola with the mixture not being thoroughly melted. The segregation bones of slag get into the wheel when slag flows through the spout of the pouring ladle and by the segregation of slags within the body of the metal. These slag bones can be avoided by exercising care in keeping slag from flowing into the pouring ladles and by scavenging or cleansing the molten iron. An alloy for cleansing the iron is recommended, which contains ¼ per cent. iron, 12 titanium, 8 boron, and 6 per cent. aluminum, silicon, etc. The titanium of this alloy combines with the occluded nitrogen, the boron fluxes out the slags, and the aluminum reduces any oxides present. In use the alloy is placed on the bottom of the pouring ladle and the molten iron run in. There is also a description of a new machine for testing car-wheels.

"Duriron": a Non-corrosive Iron Alloy. J. R. PITMAN. (*Eng. News*, lxix, 563.)—A practically non-corrosive iron alloy has recently been placed on the market under the name "Duriron." Apparently the only material which attacks it appreciably is concentrated phosphoric acid. Its composition is not given, but it is said to be 10 per cent. lighter than cast iron, which it resembles; to contain at least 10 per cent. silicon, and to have a tensile strength of 15,000 pounds and a compression strength of 70,000 pounds per square inch. Its use is chiefly in acid pipe-line fittings, valves, and in chemical and celluloid works. It is only available in the form of castings, and can only be machined by grinding.

Heat Treatment of Gun Metal. ANON. (*Amer. Mach.*, xxxviii, No. 24, 980.)—A paper presented to the British Institute of Metals on this subject states that the conclusions drawn from tests made on a metal containing 88 per cent. copper, 10 per cent. tin, and 2 per cent. zinc were as follows: No improvement may be expected from quenching, which lowers the strength of the material. Simple annealing of the metal for 30 minutes increases very considerably its strength and elongation; the maximum results being obtained after annealing at 700° C. The homogeneity and other physical properties of the metal are correspondingly improved, but particularly the capability of the castings to withstand hydraulic pressure. These results are considered to be due to the removal of the eutectic from the microstructure, which after annealing shows only the crystals of a solid solution. It is thought that this heat treatment will minimize the corrosion of the metal.

Conduction of Heat and Thermal Resistivity. C. P. RANDOLPH. (*Amer. Electrochem. Soc. Trans.*, xxi, 545.)—Investigations of the resistance to the flow of heat exhibited by various substances. These experiments were made with a view to various practical devices depending on heating by electricity. Thermal resistance is defined as the difference in temperature in degrees Centigrade per watt of heat-flow. The general conclusions are: (1) There are no materials which can be called thermal insulators in the same sense as is meant in the case of electrical insulators. (2) There is no method of preventing the flow of heat as good as an evacuated space. (3) The organic fibrous materials such as eiderdown, wool, etc., are the best insulators found. (4) Materials relatively coarse, such as poplox, may be very good insulators at low temperatures (100° C.), but have a very great negative temperature coefficient. (5) Increasing the density of a material by compression increases its resistivity. This only holds true up to a certain limit. (6) The thermal conductivity of bricks varies inversely as the temperature of burning. Details of the thermal resistivity of various organic materials, insulators containing asbestos, miscellaneous materials such as mineral wool, and ceramics, are given in a series of tables.

Metallic Beryllium (Glucinum). F. FICHTER and K. JABLCZYNSKI. (*Ber.*, xlvi, 1604.)—The metal was obtained by the electrolysis of a fused mixture of the beryllium and sodium fluorides (2 mols.: 1 mol.). The product was purified from adherent oxides by centrifuging the fine powder in a mixture of ethylene bromide and alcohol of specific gravity 1.95. It was then compressed into cylinders and fused. After fusion the metal has a specific gravity of 1.842, melts at 1280° C., and does not volatilize at 1900° C. Its electric conductivity at 20° C. is 5.41×10^4 reciprocal microhms per cubic centimetre, and its hardness is 6–7 on Mohs's scale. Its apparent inertness toward water is due to a film of oxide.

Cementing of Belts. ANON. (*Amer. Mach.*, xxxviii, No. 24, 980.)—From the *Railway and Locomotive Engineering*.—The following mixture is said to give satisfactory results: Take a good glue, add an equal weight of American isinglass, place in a glue-pot and add enough water to cover. Let the mixture soak for 10 hours, then bring it to boiling and add pure tannin until the mass appears like the white of an egg. Apply warm. Buff the grain of the leather where it is to be cemented, rub the joint surfaces solidly together, and let it dry for a few hours, when the belt will be ready for use. Tannin or tannic acid is an astringent substance used in converting hides into leather, and produces a surface on a cemented belt similar to the original leather.

Simple Method of Determining the Densities of Powdered Minerals. M. BILLY. (*Comptes Rendus*, clvi, 1065.)—In measuring the density of a powdered metal, etc., error is introduced owing to the presence of innumerable small gaseous envelopes surrounding the solid particles. To avoid this, the author replaces the air held by the powder by carbon dioxide and weighs the substance, not in water, but in an approximately normal potassium hydroxide solution, which has been previously boiled. The density of the alkaline solution alone is determined in the same way, the pycnometer being filled with carbon dioxide before the alkali is introduced. A special apparatus has been designed to facilitate these operations. The method was tested by the examination of powdered glass, the density of which had been measured prior to powdering. Whereas other methods give results accurate to about 1 part in 300, this method showed an accuracy of the same order as that of the balance employed, *viz.*, 1 in 3000. It would, therefore, seem advisable to powder all solids before measuring their density so that the absence of enclosed bubbles or fissures may be insured.

Comparison of Zinc Chloride with Coal-tar Creosote for Preserving Cross-ties. H. F. WEISS. (*Elect. Rwy. Journ.*, xli, 151.)—A great many preservatives have been tested for cross-ties, but zinc chloride and coal-tar creosote are far more extensively used than any others. These two are compared as preservatives for cross-ties, and the data do not apply to poles, piling, or other products. The most noteworthy points are: (1) Zinc chloride and coal-tar creosote, when used under normal conditions, are both effective preservatives of cross-ties, and there is little to choose between them as to the annual charges. (2) Creosoted ties generally cost initially more than Burnettized ties, the cost of treatment being two to three times as much. (3) Creosoted ties last, on an average, longer in the track than Burnettized ties, hence require less frequent renewals and changes in the road-bed. (4) If creosote advances appreciably in price the probable result will be that more ties will be treated with zinc chloride.

Fixation of Nitrogen by Alumina and Carbon. TUCKER and READ. (*Amer. Electrochem. Soc. Trans.*, xxii, 57.)—The object of the investigation was to discover whether nitrogen would combine with a heated mixture of alumina and carbon, or with the products arising from the heating of such a mixture, and to study the best conditions for effecting the reaction. The first experiments were made in a wire-wound electric resistance furnace. In order to obtain higher temperatures a granulated carbon furnace was used, through which a tube passed for holding the charge, heated by a single-phase alternating current. At first several porcelain tubes were used, embedded in the granular carbon resistor. These porcelain tubes were unable to stand the sudden changes in temperature. This was overcome by the use of a graphite tube, with a bore $\frac{5}{8}$ inch in diameter. This tube had accurately-fitted stoppers of graphite, through which the nitrogen was passed by means of metallic tubes threaded into the stoppers. The charge was contained in a graphite boat. From the result of the few experiments given it is clear that, under proper conditions, there should be no difficulty in producing aluminum nitride containing 30 per cent., or even more, nitrogen. This should be preferable to calcium cyanamide, which averages 17 to 20 per cent. fixed nitrogen.

Atmospheric Electrification during Dust Storms. V. H. JACKSON. (*Nature*, xci, 213.)—At Patna, in North India, the westerly winds, which occur in the daytime from the middle of March till June and raise a great deal of dust, are associated with a large negative potential gradient. On one occasion a negative gradient of about 1650 volts/m was measured. It is concluded that probably from 9 A.M. to 6 P.M. on the majority of days from March to June the potential gradient over a large portion of Northern India is negative and very large. This association of negative potential gradient with dust storms is similar to that found by Rudge in South Africa.

Law of Volatility in Chemical Reactions. C. MATIGNON. (*Comptes Rendus*, clvi, 1536.)—Matignon generalizes Berthollet's "law of volatility" in the following form: "Every system of liquid or solid bodies, which is capable of giving rise to a system containing volatile substances, will undergo reaction in that sense at a convenient temperature." The reaction $2\ Al + 3\ MgO = 3\ Mg + Al_2O_3$ is possible because magnesium is quite volatile at comparatively low temperatures. In the same way it is probable that barium oxide will be reduced by silicon, owing to the relative volatility of the barium produced. The law can also be extended thus: A reaction which has volatile bodies in its initial stage and also in its final stage is facilitated when the number of volatile molecules in the final stage is greater than that in the initial one,—*i.e.*, of two reactions which are equally endothermic, the one complying with this condition will take place at a lower temperature.

The Protein Substances of Yeast. P. THOMAS. (*Comptes Rendus,* clvi, 2024.)—Starting with partially-autolyzed yeast two different proteins were isolated. The first contains nitrogen 16.10 to 16.18 per cent., phosphorus 1.75 to 1.83 per cent., and sulphur 0.38 per cent., and its properties are intermediate between casein and vitellin, but more closely resemble the former. The second, which is designated *cerevisin,* appears to be a typical albumin. It contains nitrogen 16.3 to 16.4 per cent., sulphur 0.89 to 0.94 per cent., and phosphorus up to 0.7 per cent.; this phosphorus is probably present as an impurity owing to imperfect purification. Cerevisin is soluble in water and is not precipitated by acetic acid or magnesium sulphate, or by adding an equal volume of a saturated solution of ammonium sulphate to its solution. On heating the neutral or slightly acid solution it becomes turbid at about 40° C. and gives a slight coagulum at 41° C. The filtered solution remains clear up to 49° C., and yields a second coagulum at 50° C. On further heating abundant precipitation occurs between 55° and 58° C., and coagulation proceeds continuously up to 70° C. Cerevisin gives the usual precipitation and color reactions; the glyoxylic reaction (tryptophan) is particularly distinct.

The Equipment of the New Terminal Post Office in New York. L. B. MARKS and J. E. WOODWELL. (*Electr. World,* lxi, 39.)—Herein is described the electrical and mechanical equipment, wiring and illumination of the Government building over the Pennsylvania Railroad yards. The total volume of business in the building will eventually represent an average of over 5,000,000 pieces of mail matter daily, which is about double the present amount. Two classes of machinery are provided—one for handling the outgoing and one for the incoming mail. There are eight overhead belt conveyors for the outgoing mail, driven by motors of the semi-enclosed type, designed for 650 volts. There are two sources of energy for operating the mail handling motors, one consisting of separate feeders from the main switchboard in the power plant, and the other of a connection taken from the third rail operating the train service. The electrical equipment of the post office consists of a complete system of conduits and wiring for lighting and motor service, with feeders and meter switchboard and separate distributing switchboards. Details are supplied.

Alum Mountain in New Mexico. ANON. (*Chem. Trade J.,* June 21, 1913.)—The alum mountain near the Gila River, in southwestern New Mexico, is 900 feet high, and covers two square miles, and the United States Geological Survey finds it to be so pure that for many uses it can be marketed in the natural state. As a probable future source of aluminum this material has a still greater value. Enormous beds of lignite near-by offer power at one-fourth to one-half the cost of hydro-electric power.

Separation of Graphite from Iron-Silicon Alloys. G. CHARPY and A. CORNU. (*Comptes Rendus*, clvi, 1616.)—Silicon in steels, as in pig iron, facilitates the separation of the carbon as graphite when the alloy is heated to a suitable temperature. The phenomenon is, however, complicated in steels by the fact that the total carbon may be lower than the maximum quantity that the steel is capable of dissolving at a high temperature. The separation of graphite in this way from a steel is therefore observable through a range of temperature rising from T°, the temperature at which separation begins, and which is lower as the percentage of silicon is higher, to T'°, at which the solubility of graphite in steel corresponds to the total carbon present, and which is higher as the percentage, not only of carbon but also of silicon, is higher. In steels low both in carbon and silicon T' may be below T, and then no separation of graphite occurs.

Aërodynamics. A. LECHNER. (*Phys. Zeitschr.*, xiv, 210.)—Determines both theoretically and experimentally the "phygoid" or trajectory of a flying model for the case when it moves in a liquid. The phygoid theory is directly applicable to liquids if the laws of resistance are the same as in air. The paths can either be circles or waves, according to the initial velocity and direction, and in the case of instability "tumbling" curves will be obtained. This was verified by means of flying models of thin sheet metal cut out in the rough outline of birds and tipped with lead. These were released in or projected into water.

Pressure in the Solar Atmosphere. C. E. ST. JOHN. (*Science*, xxxvii, 28.)—An investigation involving the comparison of arc and solar spectra of iron is being undertaken at the Mount Wilson Solar Observatory with the 150-foot Tower telescope. The preliminary results show that the solar lines of iron, classified in accordance with their displacement in the solar spectrum, fall into the classes suggested by Gale and Adams in their study of pressure-shift under laboratory conditions, and indicate pressures in the solar atmosphere varying from 0.7 to 6.5 terrestrial atmospheres for the different groups.

Preparation of Molybdenum and Tungsten Carbides. S. HILPERT and M. ORNSTEIN. (*Ber.*, xlvi, 1669.)—The carbides of molybdenum and tungsten can be obtained by heating the finely-powdered metals, or their tri-oxides, in a current of carbon monoxides or of a mixture of methane and hydrogen (1 : 1 by volume). By the action of carbon monoxide on molybdenum at 600° and 1000° C., Mo_2C is obtained; at 800° C. products ranging from MoC to Mo_2C_3 are obtained. Tungsten yields W_3C_4 by the action of carbon monoxide at 1000° C., and WC by the action of methane and hydrogen at 800° C.

Hertzian Oscillations from Cathode. K. BIRKELAND. (*Comptes Rend.*, clvi, 879.)—Electrical oscillations are found to be produced by the intermittent discharge emanating from isolated spots on the cathode of a Crookes tube.

Lag in the Combustion of Gaseous Mixtures. TAFFANEL and LE FLOCH. (*Comptes Rend.*, clvi, 1544.)—The occurrence of lag in the inflammation of methane-air mixtures is not due to the presence or absence of moisture. The probable cause is the relatively slow rate at which the velocity of reaction increases with the temperature compared with the rate in other inflammable mixtures which do not exhibit the lag.

Tri-Ferrous Carbide (Cementite). O. RUPP and E. GERSTEN. (*Ber.*, xlv, 63.)—Pure cementite was prepared by heating a γ-iron, containing 4 per cent. of carbon and very free from impurities, to whiteness for an hour with powdered carbon. Analysis showed it to contain 93.28 per cent. of iron and 6.69 per cent. of carbon (theory 93.33 and 6.67). It was a dark-gray or bronze-colored substance, consisting of sphœrolithic aggregates of needle-like crystals, extremely brittle, and with a hardness slightly above that of calcite (whence it follows that the hardness of chilled irons is not due to cementite as such, but to its solid solution in γ-iron). Its specific gravity was 7.396, and specific volume 24.34, while that calculated from the specific volumes of its constituents is 27.84, showing that contraction occurs during its formation. To determine its heat of formation it was burnt in oxygen in a bomb calorimeter, $Fe_3C + 3O_2 = Fe_3O_4 + CO_2$, the product analyzed and allowance made for the amount of iron burnt only to ferrous oxide: the result per gram-molecule was 375.1 calories. The heat of combustion of iron to ferroso-ferric oxide was similarly determined for two specimens, with results agreeing closely among themselves and in good accord with Berthelot's figure obtained by a totally different method: per gram-molecule 265.2 calories. Adding to this the heat evolved in the combustion of an atom of graphite carbon to carbon dioxide, 94.8 calories, we get 360 calories as the sum of the heat of combustion of the separate constituents of cementite. Hence cementite is endothermic, and the reaction $Fe_3 + C = Fe_3C$ absorbs 15.1 calories. This is entirely at variance with Campbell's result, which was confirmed by the calculations of Schenk, Semiller, and Falcke, but confirms a deduction of Ruff's from a study of the equilibrium diagram of the iron-carbon alloys.

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